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(54) Title: METHOD FOR CONSTRUCTION OF NANOTUBE MATRIX MATERIAL		
(57) Abstract		
<p>A method of constructing nanotube matrix material in a controlled manner wherein, a nanotube fragment having at least two potential energy-binding surfaces including two distinct levels of binding potential energy of H-bonding and a second lower binding potential energy of covalent bonding, are used for binding corresponding nanotube fragments. The method comprises the steps of: (a) bringing a solution of nanotube fragments together; (b) heating the solution to a temperature to disrupt the H-bonding but insufficient to denature the covalent bonding; (c) agitating the solution and slowly reducing the temperature (annealing) to a temperature where the H-bondings are stable, producing an optimal configuration; (d) adding a reagent to the solution to cause ring closure; and (e) introducing a catalytic element for purification and dehydrogenation of the nanotube matrix material formed.</p>		
<p style="text-align: center;">Zigzag precursor synthesis</p> <p>The diagram illustrates the 'Zigzag precursor synthesis' process. It begins with two separate phenanthrene-based molecules, labeled 60 and 61. Molecule 60 is described as 'Synthesize phenanthrene based molecule 1' and molecule 61 as 'Synthesize phenanthrene based molecule 2'. These molecules are then combined in a step labeled 'Mix and anneal' (63). This step shows two possible arrangements of the molecules: an 'Allowed arrangement' (64) and an arrangement that is 'This arrangement is prevented'. The 'Allowed arrangement' shows the molecules stacked in a way that their binding surfaces (labeled A, B, and C) align correctly. The 'Prevented arrangement' shows a misalignment. Finally, a reagent is added to cause ring closure (65), resulting in a closed nanotube matrix structure.</p>		

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METHOD FOR CONSTRUCTION OF NANOTUBE MATRIX MATERIAL

Field of the Invention

5 The present invention relates to the creation of complex material and/or electronic structures and, in particular, discloses the creation of a nanotube matrix material.

Background of the Invention

10 The use of materials in a mechanical manner and electronic is fundamental to society. Different materials such as steel and carbon fibre are well sought after for their mechanical strength to weight characteristics. Additionally, new materials having new improved properties are always desirable. Also materials having unique
15 electrical properties are also highly desirable where they have a high degree of utility.

Further, in recent years, a huge industry has been created in the fabrication of integrated circuit type devices on silicon wafers etc. Huge research investments
20 continue to be made in the continued miniaturization of electronic circuits and the building up of complex 3 dimensional structures layer by layer on a semiconductor wafer.

In 1991, Sumio Iijima reported the discovery of carbon
25 nanotube type devices. The discovery of carbon nanotubes has been recognised as a new fascinating material with nanometre dimensions and promising exciting new areas of carbon chemistry and physics.

For a series of background articles on the application
30 of carbon nanotube type devices, reference is made to the text "carbon nanotubes" edited by Endo, Iijima and Dressel Haus published 1996 by Elsevier Science Limited. The publication contained a number of survey articles covering the field.

35 Unfortunately, the construction of nanotube type devices proceeds in a somewhat haphazard and uncontrolled

manner. Nanotubes are known to be formed in a DC arc discharge or the catalytic composition of acetylene in the presence of various supported transition metal catalysts.

Unfortunately, such arrangements tend to lead to
5 disordered forms of carbon nanotubes which limits their utility through the limitation of the ability to construct complex devices from the nanotubes.

Summary of the Invention

It is an object of the present invention to provide
10 for an effective form of synthesis of complex material structures such as nanotube devices in a controlled manner.

In accordance with a first aspect of the present invention, there is provided a method of constructing a structure from intermediate parts, each of the parts
15 including at least two potential energy binding surfaces each surfaces having at least two levels of binding potential energy for binding with another corresponding intermediate part, the binding energy including a first intermediate binding potential energy and a second lower
20 binding potential energy, the method comprising the steps of: (a) bringing a series of intermediate parts together in a collation of intermediate parts; (b) agitating the collation to an average energy exceeding the intermediate binding energy; (c) slowly lowering the average energy to a
25 level substantially at the first intermediate binding potential energy; (d) introducing a catalytic element to the collation to cause the parts to bind at substantially the second lower potential energy so as to form the structure.

30 The method can further comprise the step of iteratively repeating steps (a) to (d) to form other structures.

The intermediate parts can comprise molecules and the first intermediate binding potential energy can comprise
35 substantially hydrogen bonding of the intermediate parts and the second lower potential energy can comprise covalent

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bonding of the parts. The agitating step can comprise heating or ultrasonically agitating the collation.

The parts can include nanotube fragments with portions having one of resistor, diode or transistor device characteristics.

The structure can comprise a 3 dimensional interconnected array of nanotube fragments and can include a series of nanotube rods interconnected with nanotube hub components. The nanotube fragments can include a series of protuberances formed on an outer non-reactive surface thereof so as to reduce Van der Walls interactions.

In accordance with a further aspect of the present invention, there is provided a nanotube structure comprising a matrix of interconnected tetrahedral or cubic nanotube junctions. The interconnect can comprise a nanotube strut portion.

In accordance with a further aspect of the present invention, there is provided a method of constructing nanotube components interconnected to a fullerene or other hub component.

In accordance with a further aspect of the present invention, there is provided a method of constructing a hub component for interconnecting multiple nanotube components.

In accordance with a further aspect of the present invention, there is provided a method of constructing a low density nanotube crystal.

In accordance with a further aspect of the present invention, there is provided an electrical device having controlled resistive properties comprising: a central nanotube of a zigzag type of a predetermined length interconnected between two nanotubes of an armchair type.

In accordance with a further aspect of the present invention, there is provided an electrical device having signal amplification properties comprising: a central nanotube of a zigzag type interconnected between two nanotubes of an armchair type; field application means for

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applying a field to the central nanotube, thereby altering the conductive path between the armchair type nanotubes.

In accordance with a further aspect of the present invention, there is provided an electrical device having
5 signal amplification properties comprising: a central nanotube of a zigzag type interconnected between two nanotubes of an armchair type; and a control nanotube of a zigzag type interconnect to the central nanotube, the control nanotube being interconnected to a field
10 application means for applying a voltage to the central nanotube, thereby altering the conductive path between the armchair type nanotubes.

In accordance with a further aspect of the present invention, there is provided an electrical device
15 comprising a series of nanotubes interconnected at a common junction, the nanotubes, at the junction, comprising zigzag nanotubes, and a predetermined number of the nanotubes including a circumferential join to an armchair type nanotube so as to provide for the operational
20 characteristics of the device.

At least one of the armchair type nanotubes are preferably further interconnected to a common junction of armchair type nanotubes.

In accordance with a further aspect of the present
25 invention, there is provided an electrical device comprising a series of nanotubes interconnected at a common junction, the nanotubes, at the junction, comprising zigzag nanotubes, and a predetermined number of the nanotubes including a circumferential join to an armchair type
30 nanotube so as to provide for the operational characteristics of the device.

In accordance with a further aspect of the present invention, there is provided an electrical device comprising a series of armchair type nanotubes
35 interconnected to a common junction.

In accordance with a further aspect of the present invention, there is provided an electrical device comprising the interconnection of a labyrinth of nanotube devices via common junctions, the devices including a series of diode elements formed from the interconnection of nanotubes of different dimensions.

In accordance with a further aspect of the present invention, there is provided an electrical device comprising a quantum well structure including the junction of a series of metallic type nanotube structures attached to a semiconductive nanotube so that electrons are substantially captured in the junction.

In accordance with a further aspect of the present invention, there is provided an electric device comprising a ballistic electron nanotube device including a nanotube junction with at least one quantum well structure adjacent the junction.

In accordance with a further aspect of the present invention, there is provided a method of constructing precursor synthesis components for forming nanotube fragments.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Fig. 1 illustrates a carbon nanotube diode formed by a linear junction between armchair and zigzag nanotubes;

Fig. 2 and Fig. 3 illustrate a nanotube resistive element;

Fig. 4 illustrates a nanotube bipolar type element;

Fig. 5 to Fig. 7 illustrate various views of a core building block for building cubic nanotube structures;

Fig. 8 illustrates a core building block for building tetrahedral structures;

Fig. 9 illustrates a portion of a tetrahedral structure;

Fig. 11 and Fig. 12 illustrate a four junction nanotube structure;

5 Fig. 13 to Fig. 15 illustrate various nanotube arrays built from elements shown in Fig. 11 and Fig. 12;

Fig. 16 illustrates the density of a nanotube mesh for different lengths of strut benzene units;

10 Fig. 17 illustrates a ballistic electron flow transistor structure;

Fig. 18 illustrates the process of zigzag precursor synthesis;

Fig. 19 illustrates the process of armchair (8,8) precursor synthesis;

15 Fig. 20 illustrates the process of double ended zigzag precursor synthesis;

Fig. 21 illustrates the process of double ended zigzag nanotube synthesis;

20 Fig. 22 illustrates the process of zigzag nanotube synthesis;

Fig. 23 illustrates the process of functionalization and protection of an end of a nanotube fragment;

Fig. 24 illustrates the process of nanotube linear diode synthesis;

25 Fig. 25 illustrates the process of increasing the length of an armchair nanotube;

Fig. 26 illustrates the process of further increasing the length of an armchair nanotube;

30 Fig. 27 illustrates the process of synthesis of nanotube rods;

Fig. 28 illustrates the process of synthesis of nanotube rods with end joiners;

Fig. 29 illustrates a first method of joining 'balls' to nanotube rods;

35 Fig. 30 illustrates the process of synthesis of a low density nanotube crystal;

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Fig. 31 illustrates a low density nanotube crystal;

Fig. 32 illustrates an alternative form of formation of a nanotube crystal array hub component starting material;

5 Fig. 33 illustrates the process of forming hub components;

Fig. 34 illustrates the 'dumbbell' synthesis process;

Fig. 35 illustrates an alternative process for forming a nanotube crystal;

10 Fig. 36 illustrates the problem of nanotube - nanotube attraction; and

Fig. 37 illustrates a modified form of nanotube.

Description of Preferred and Other Embodiments

The preferred embodiment discloses a method of
15 manufacture of complex nanotube matrix arrays from intermediate components. Whilst particular descriptions will be given, it will be evident to those skilled in the art that the teachings of the preferred embodiment can be extended to the construction of arbitrary nanotube type
20 devices made up of the placement of components at arbitrary locations.

The electronic devices can include diodes, transistors, resistors etc of a 3-Dimensional form. A number of these devices will now be discussed with
25 reference to Fig. 1 to Fig. 17.

In Fig. 1, there is illustrated a nanotube fragment 1 which includes an "armchair" nanotube 2 interconnected to a zigzag type nanotube wherein at the junctions 4 a diode structure is formed. This results of uneven charged
30 distribution around the junction 3 allowing the device to operate as a diode.

In Figs. 2 and 3, there is illustrated a tunnelling resistor type device which can be formed from two armchair type nanotubes 6, 8 surrounding a central zigzag type
35 nanotube of various lengths 7, 9. The breakdown voltage of the arrangement of Fig. 2 and 3 is approximately two volts

when carbon nanotubes are utilized in about 6 volts when boron-nitride nanotubes are utilized.

Turning to Fig. 4, there is illustrated a bipolar type transistor 11 which is similar to the structure of Fig. 3 but for the inclusion of a third arm 10 which can be electrically driven to a state so as to control the current flow along the other arms 12, 13.

The bipolar type transistor 11 of Fig. 4 is normally non conductive of ballistic transistors due to a band gap mismatch. The application of a voltage potential via the junction 10 results in a band shifting resulting in band gap matching for ballistic transport. The application of potential via arm 10 will also result in a leakage current.

The transistor complex of Fig. 4 can be extended to a network complex. Turning to Figs. 5 to Fig. 7, there is shown a basic element of the network complex which includes a set of six back to back diodes. Of course, other forms of arms can be formed so as to provide for direct connections, diodes, quantum dots etc. The network element shown in different views in Fig. 5 to Fig. 7 can be utilised in a cubic network matrix. Of course, other network matrices are possible. For example, in Fig. 8, there is shown a tetrahedral type components 20 - 22 which can be used to form a corresponding matrix 23 as illustrated in Fig. 9. The matrix arrangement includes conducting pathways 24, 25 and transistor element 26. The arrangement 23 of Fig. 9 being further constructed into a tetrahedral mesh in accordance with circuitry requirements.

Other arrangements are also possible. Turning now to Fig. 10, there is illustrated a quantum dot arrangement in a tetrahedral lattice with the "metallic" core nanotube portion 30 being surrounded by a series of zigzag type nanotube arms eg 31. An electron pushed into the centralised core 30 will be in turn trapped there.

Turning now to Figs. 11 and 12, there is illustrated an alternate tetrahedral junction 35 which is formed having

sp³ carbon at each junction. The arrangement has no inherent charge because it is alternate and it is formed from an sp³ arrangement. The element 33 can be utilised as a structural element with various structural arrangements illustrated in Fig. 13 to Fig. 15. The structural arrangements have a number of important advantageous characteristics. For example, Fig. 16 illustrates a graph of the resulting density for different strut lengths of a basic element. (The strut length being twice the length shown on the graph). The graph of Fig. 16 being for (18,0) type nanotubes. The likely mechanical properties therefore of structures such as those illustrated in Figs. 13 to Fig. 15 include excellent high strength, high elasticity, high stretch, high compression and high twist. However, the arrangements are likely to have a low resistance to shear. Arrangements disclosed hereinafter can be provided having a higher resistance to shear.

Turning now to Figs. 17 there is illustrated a view of a modified transistor type junction element 50. In this case, the arms 52,53 have been modified so as to include Boron Nitride bands eg. 54,55 and 58,59 which act as a quantum dot trap on either side of the arms eg 56,57 which in turn can allow for ballistic electron flow. The ballistic electron flow is effected by the quantum dot trap on either side and the quantum dot trap therefore controls the reflection of electrons flowing along the ballistic electron flow channels 56, 57. The arrangement of Fig. 17, through the utilisation of quantum dot structures, dramatically reduces the likely gate current in comparison to the arrangement of Fig. 4. The arrangement 50 of Fig. 17 can be utilised as a multi level memory and the arms eg. 52,53, 56,57 can be constructed in many different combinations through different functionalisations leading to a plethora of different capabilities.

A method of formation of complex 3 dimensional matrices containing the aforementioned devices in a

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predetermined arrangement will now be discussed.

Turning initially to Fig. 18, there will now be discussed the steps in forming a zigzag nanotube precursor element.

The first step is to prepare two molecules 60, 61 which are
5 synthetically accessible using standard organic chemistry techniques. Both molecules are considered as having four sides. Three of the sides contain hydrogen bonding
moieties which are used at a later stage of the synthesis. These are protected with three orthogonal protecting
10 groups, labelled A,B and C. The fourth side has a hydrogen bonding pattern which is complementary between the two molecules. This pattern must be asymmetrical, to prevent reverse attachment.

The two elements 60,61 are mixed and annealed to allow
15 an interconnection 63 which is later closed 64 so as to form a final product 65. This can be followed by dehydrogenation and purification. Dehydrogenation can occur using, for example, a palladium catalyst. Although dehydrogenation is shown at every major stage. In most
20 cases, dehydrogenation will not be necessary until the final step in the entire synthesis.

Purify the product to separate it from any remaining unjoined fragments and ring closure reagent. There is a
substantial difference in molecular weight between the
25 reagents and the product, so various forms of purification can be used.

Turning now to Fig. 19, there is illustrated the process of armchair (8,8) precursor synthesis. The first
step is to prepare two molecules 70,71 which are
30 synthetically accessible using standard organic chemistry techniques. Both molecules are considered as having four sides. Three of the sides contain hydrogen bonding
moieties which are used at a later stage of the synthesis. These are protected with three orthogonal protecting
35 groups, labelled A,B and C. The fourth side has a hydrogen bonding pattern which is complementary between the two

molecules. This pattern must be asymmetrical, to prevent reverse attachment.

The result is mixed 72 and annealed 73 and a reagent is added to cause ring closure so as to form precursor
5 fragment 74.

Fig. 20 illustrates the process of double ended (16, 0) nanotube precursor synthesis. The first step is to prepare two molecules 80,81 which are synthetically accessible using standard organic chemistry techniques.
10 Both molecules are considered as having four sides. Three of the sides contain hydrogen bonding moieties which are used at a later stage of the synthesis. These are protected with three orthogonal protecting groups, labelled A,B and C. The fourth side has a hydrogen bonding pattern
15 which is complementary between the two molecules. This pattern must be asymmetrical, to prevent reverse attachment.

The result is mixed 83 and annealed 84 and a reagent is added to cause ring closure 85.

20 The aforementioned fragments can then be utilized in forming various nanotube segments as will be described in further detail hereinafter.

Turning initially to Fig. 21, there is illustrated the process of forming double ended zigzag (16, 0 nanotube fragments). Starting with a functionalised PAH 90,91 such as benzol [G,H,I] perylene having functionalised end
25 portions 92,93, a solution of such components 93 is heated to a temperature sufficient to disrupt the hydrogen bonding but insufficient to denature any covalent bonds. The solution is then agitated and slowly reduced in temperature
30 (annealed) to a temperature where the hydrogen bonds are highly stable. This process anneals the fragments into their optimal configuration 94 which comprises a loop component. A reagent is then added to the mix so as to
35 cause ring closure 95. Subsequent dehydrogenation can occur using, for example, a palladium catalyst. Subsequent

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purification can separate the product 96 from any remaining unjoined fragments and any reagents.

Turning now to Fig. 22, there will now be described a process of fabrication of zigzag (16, 0) nanotube components. Starting with a zigzag precursor molecule 101 having functionalized end portions 102-105 the end portions 104, 105 are de-protected 106, 107. A solution 108 of the components is heated to a temperature sufficient to disrupt the hydrogen bonding but insufficient to denature any covalent bonds. The annealing temperature is slowly reduced to a point where the hydrogen bonds are highly stable. The process anneals the fragments into their optimal configuration 109 - 112. Subsequently, a reagent is added to cause ring closure 113. Finally, the elements 113 are dehydrogenated using, for example, a palladium catalyst. Subsequent purification steps can separate the product from any remaining unjoined fragments and ring closure reagent.

It will be readily evident that the abovementioned synthesis process can also be applied to other nanotube fragments of different chirality.

Turning to Fig. 23, there is illustrated an example nanotube fragment 120 in more detail. The fragment can comprise the graphitic layer 121 followed by a reactive oxygen layer 122 which is masked by an isopropyl termination layer 123.

The aforementioned techniques of construction of nanotube components can be extended to provide for other nanotube structures such as diodes etc. and a number of structures will now be described.

Starting with Fig. 24, which shows a process of synthesis of nanotube linear diodes the starting material can include separately synthesised nanotube components 130, 131 with the components 130 being armchair nanotube fragments and the components 131 being zigzag-type nanotube components. Each of the components 130, 131 having

protected ends. The first step being to de-protect the end B of the armchair nanotube 130 and the end A of the zigzag nanotube 131 to form nanotube components 132 and 133. The nanotubes having de-protected ends are then mixed in a solution 134 and the solution allowed to slowly anneal starting at a temperature sufficient to disrupt the hydrogen bond but insufficient to denature any covalent bonds and finishing at a temperature where the hydrogen bonding is highly stable 135. Next, a reagent is added so as to ensure closure 136 and the result dehydrogenated using, for example, a palladium catalyst. The solution can then be purified to separate the diode product from any remaining unjoined fragments and ring closure reagents.

Turning now to Fig. 25, there is illustrated a method of increasing the length of a nanotube component. Starting initially with a quantity of nanotube fragments 140, with half of the fragments, the B end is de-protected 141 and with the other half of the fragments A end is de-protected 142. The two halves are mixed 143 and slowly annealed starting at a room temperature sufficient to disrupt the hydrogen bonds but insufficient to denature any covalent bonds and finishing at a temperature where the hydrogen bonding is highly stable 145. Subsequently, a reagent is added to cause ring closure with subsequent dehydrogenation occurring.

Turning now to Fig. 26, there is illustrated a process of extending a length of a nanotube fragment. Starting initially was a quantity of nanotube fragments 150 with complimentary hydrogen bonding ends, both ends are protected. With half the fragments, the end B is de-protected 151 and with the other half of the fragments, the end A is de-protected 152. The two halves mixed 153 and slowly annealed 154 starting at a temperature sufficient to disrupt the hydrogen bonds but insufficient to denature any covalent bonds and finishing at a temperature where hydrogen bonding is highly stable 155. A reagent is then

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added so as to cause ring closure 156.

Turning now to Fig. 27, there is illustrated a process of extending the length of nanotube fragment. In this process, two nanotube fragments 161 and 162 are de-protected 164, 165 before being mixed together 166. The mixture is slowly annealed 167 and a reagent added 168 causing ring closure with the final result 169 including optional dehydrogenation and purification. The aforementioned process can be utilized to build up a arbitrary 3 dimensional mesh of nanotube type components. Turning now to Fig. 28, there is illustrated a process of synthesis of nanotube rods having capped ends. Initially,

A quantity of nanotube fragments 170 are utilized having complementary hydrogen bonding ends and both sides protected. Half of the fragments 170 have a first end de-protected 171 with the other half of the fragments 172 having their second end de-protected. A capping unit 173, 174 which can be synthesised using similar methods to the initial nanotube segment synthesis, to the corresponding mixture 173, 174 and the mixture annealed. The subsequent closing 175, 176 proceeds in the usual manner. The rods formed by the process described in Fig. 28 can then be matched with corresponding "balls" to form an overall matrix. One form of formation of the "balls" and rods will be described with reference to Fig. 29. Subsequently, the other end is de-protected eg. 177, 178 and the two mixtures are added together and annealed 179 so as to form loosely bound structures 179 which are subsequently closed and dehydrogenated 180.

Turning now to Fig. 29, there is illustrated the processing steps in one method of construction of components in creating a matrix. The first step is to functionalise 181 a buckyball 182 by attracting a hydrogen bonding moiety to each of the 12 five member rings of the buckyball. The nanotube components (180 of Fig. 28) are then mixed with the functionalised buckyballs 181. The

concentration of buckyballs should be much more than double that of the nanotubes, to minimise the occurrence of more than one rod attaching to a single buckyball. The hydrogen bonding is allowed to go to completion 183 and a reagent
5 added to convert the hydrogen bond to covalent bonds 184. Finally, the rods are purified 185 to eliminate any molecules which contain more than one rod in addition to eliminating any individual leftover buckyballs and bonding reagent.

10 Next, as illustrated in Fig. 30, a mixture of nanotubes 180 and nanotubes with covalently bonded functionalised buckyballs on the ends 185 is provided. Preferably, exactly 8.33% of nanotubes 120 are provided in the mixing ratio. A dilute solution of nanotube rods is
15 prepared with 11 of every 12 rods having no buckyball termination while the remaining 12 have a buckyball termination at both ends. The volume of solvent is preferably greater than the volume of the desired expanded nanotube mesh. The nanotube mesh is then annealed very
20 slowly so as to form a mesh 187 as illustrated in Fig. 31. The hydrogen bonded interaction with the buckyball must be strong enough to allow for self assembly of the matrix 187. The slow annealing allows a smaller hydrogen bond energy. After annealing, a reagent is added which converts the
25 hydrogen bonds to covalent bonds. Finally, the solvent is drained and the structure 187 is filled with an inert gas.

Alternatively, a different mesh can be formed through the utilisation of an alternative hub components to the buckyball hub 181 components as previously shown in Fig.
30 29. The alternative arrangement begins with the synthesis of hub fragments as illustrated in Fig. 32. The hub fragments 190 can be synthesised using organic synthesis techniques. The fragments can be functionalized with complementary patterns of hydrogen bonding moieties on two
35 sides of the PAH.

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On a third side is a pattern of hydrogen bonding moieties which is complementary to that used on one end of compatible nanotube fragments. This is shown protected with B. The forth side has a rotational self-complementary pattern of hydrogen bonding moieties, which are protected with the orthogonal protecting groups A. A solution of components 191 is then heated to a temperature sufficient to disrupt the hydrogen bonds but insufficient to denature any covalent bonds. The temperature is slowly reduced to a point where the hydrogen bonds are highly stable. This results with the formation of fragments 192. A reagent is then added so as to form final hub fragments 193.

The hub fragments are then formed into hub units as illustrated in Fig. 33. A hub unit 204 is constructed from 12 hub fragments 193. The first step 200 is to de-protect the reactive component of a large number of hub fragments and add them into a solution 201 which is heated to a temperature sufficient to disrupt the hydrogen bonds but insufficient to denature any covalent bonds. The fragments are annealed such that 12 hub fragments form a cluster with the fragments evenly distributed over the surface. The typological interconnection is illustrated 203 with a "perspective" 204 of a single hub being also provided. A reagent is added to cause ring closure and optional dehydrogenation is carried out followed by purification.

An alternative synthetic route may be to use a functionalised C_{60} buckyball as a "guide" to spherical clustered hub formation with the buckyball remaining inside the hub.

Next, "dumbbell" units can be formed using the process as illustrated in Fig. 34. The dumbbell units are formed through providing a mixture of synthesised hubs 204 and double ended rods 210 utilizing the synthesis indicated. The ends of each of the hubs and rods are de-protected 210, 212. A mixture of hubs and rods is provided whereby the molar concentration of hubs is much greater than twice

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the molar concentration of rods. This minimises the probability of two rods joining the same hub.

Subsequently, a reagent is added to close the rings and optional dehydrogenation is carried out followed by
5 purification so as to provide for a collection of purified dumbbell units 213.

Turning now to Fig. 35, there is illustrated the steps required in the synthesis of a low density high strength nanotube crystal which can be synthesized from dumbbell
10 components 213 (of Fig. 34) in addition to a series of double ended rods 220 which are de-protected 221 and added in solution with the double units 213. The mixture of dumbbells and rods is accurately controlled in a molar ratio of 11 rods to each dumbbell. A face centred cubic crystal
15 of nanotube lattice may be created in a process analogous to Czochralski crystal growing. In this case, nanotube dumbbells and rods are analogous to the atoms in Czochralski crystal growth. The nanotube solution is heated from below to a temperature which is slightly above the hydrogen
20 bond disassociation temperature. A seed crystal is lowered into this solution and slowly pulled out. Nanotubes are crystallised on the seed as the temperature falls at the melt interface in the process of pulling the crystal. The seed is preferably rotated so that the
25 nanotubes of orthogonal orientation are not preferentially depleted in the "melt". The lattice drains of solvent as the crystal is pulled. In an alternative arrangement an initial seed can be generated by patterning a planer surface with dumbbell attracting spots at the same pitch as
30 the crystal lattice.

After the crystal is pulled it can be lowered into clean solvent which contains a ring closing reagent and a dehydrogenation catalyst. Since all hydrogen bonds have
35 been replaced by covalent bonds, and dehydrogenated, the structure is fully aromatic and achieves its full strength. The final structure being illustrated 225.

It will be evident that the forgoing teachings in the construction of large mesh structures can be readily modified in many way whilst still falling within the spirit and scope of the present invention.

5 For example, a matrix structure having predetermined electrical devices can be constructed by forming the electrical components and substituting the components at predetermined points of the mixing and annealing process. It will be further evident that the annealing process can
10 also be utilized in the creation of other complex interlinked structures.

 Further, the nanotube rod components utilized in forming structures can include a number of refinements. In particular, due to the interaction of Van der Waals
15 attractive forces in solution, the nanotube components themselves may exhibit a high degree of attractiveness between components. Such a situation is illustrated in Fig. 36 with the nanotube fragments 230 and 231 exhibiting a high attractiveness which can lead to the formation of
20 intertwined strands of nanotube components.

 One form of reduction of the effect of Van Der Walls attraction is shown in Fig. 37 wherein a series of methane groupings e.g. 235, 236 are formed on the outer walls of the nanotubes so as to provide for a reduction in the
25 opportunity for Van der Walls interaction between the tubes 237, 238.

 It would be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific
30 embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

We Claim:

1. A method of constructing a structure from intermediate parts, each of said parts including at least two potential energy binding surfaces each surfaces having at least two levels of binding potential energy for binding with another corresponding intermediate part, said binding energy including a first intermediate binding potential energy and a second lower binding potential energy, said method comprising the steps of:
 - (a) bringing a series of intermediate parts together in a collation of intermediate parts;
 - (b) agitating said collation to an average energy exceeding said intermediate binding energy;
 - (c) slowly lowering said average energy to a level substantially at said first intermediate binding potential energy;
 - (d) introducing a catalytic element to said collation to cause said parts to bind at substantially said second lower potential energy so as to form said structure.
2. A method as claimed in claim 1 further comprising:
 - iteratively repeating steps (a) to (d).
3. A method as claimed in claim 2 wherein said intermediate parts comprise molecules and said first intermediate binding potential energy comprise substantially hydrogen bonding of said intermediate parts and said second lower potential energy comprises covalent bonding of said parts.
4. A method as claimed in any previous claim wherein said agitating step comprises heating or ultrasonically agitating said collation.
5. A method as claimed in any previous claim wherein said parts include nanotube fragments.
6. A method as claimed in claim 5 wherein said nanotube fragments include portions having one of resistor, diode or transistor device characteristics.

7. A method as claimed in any previous claim 4 to claim 6 wherein said structure comprises a 3 dimensional interconnected array of nanotube fragments.

8. A method as claimed in any previous claim wherein
5 said structure includes a series of nanotube rods interconnected with nanotube hub components.

9. A method as claimed in any previous claim 4 to 7 wherein said nanotube fragments include a series of protuberances formed on an outer non-reactive surface
10 thereof.

10. A structure when formed in accordance with the method as set out in any of claims 1 to 9.

11. A nanotube structure comprising a matrix of interconnected tetrahedral or cubic nanotube junctions.

12. A nanotube structure as claimed in claim 11
15 wherein said interconnect comprises a nanotube strut portion.

13. A nanotube structure comprising a series of nanotube interconnected with fullerene interconnection
20 components.

14. A method of constructing nanotube components interconnected to a buckyball or other hub component.

15. A method of constructing a hub component for interconnecting multiple nanotube components.

16. A method of constructing a low density nanotube
25 crystal.

17. An electrical device having controlled resistive properties comprising:

a central nanotube of a zigzag type of a
30 predetermined length interconnected between two nanotubes of an armchair type.

18. An electrical device having signal amplification properties comprising:

a central nanotube of a zigzag type
35 interconnected between two nanotubes of an armchair type;

- 21 -

field application means for applying a field to said central nanotube, thereby altering the conductive path between said armchair type nanotubes.

19. An electrical device having signal amplification
5 properties comprising:

a central nanotube of a zigzag type
interconnected between two nanotubes of an armchair type;
and

a control nanotube of a zigzag type interconnect
10 to said central nanotube, said control nanotube being
interconnected to a field application means for applying a
voltage to said central nanotube, thereby altering the
conductive path between said armchair type nanotubes.

20. An electrical device comprising a series of
15 nanotubes interconnected at a common junction, said
nanotubes, at said junction, comprising zigzag nanotubes,
and a predetermined number of said nanotubes including a
circumferential join to an armchair type nanotube so as to
provide for the operational characteristics of said device.

20 21. An electrical device as claimed in claim 20
wherein at least one of said armchair type nanotubes are
further interconnected to a common junction of armchair
type nanotubes.

22. An electrical device comprising a series of
25 nanotubes interconnected at a common junction, said
nanotubes, at said junction, comprising zigzag nanotubes,
and a predetermined number of said nanotubes including a
circumferential join to an armchair type nanotube so as to
provide for the operational characteristics of said device.

30 23. An electrical device comprising a series of
armchair type nanotubes interconnected to a common
junction.

24. An electrical device comprising the
interconnection of a labyrinth of nanotube devices via
35 common junctions, said devices including a series of diode
elements formed from the interconnection of nanotubes of

- 22 -

different dimensions.

25. An electrical device comprising a quantum well structure including the junction of a series of metallic type nanotube structures attached to a semiconductive
5 nanotube so that electrons are substantially captured in said junction.

26. An electric device comprising a ballistic electron nanotube device including a nanotube junction with at least one quantum well structure adjacent the junction.

10 27. A method of constructing any of the electrical devices as set out in claims 17 to 26 utilizing the method of any of claims 1 to 9.

28. A method of constructing precursor synthesis components for forming nanotube fragments substantially as
15 hereinbefore described.

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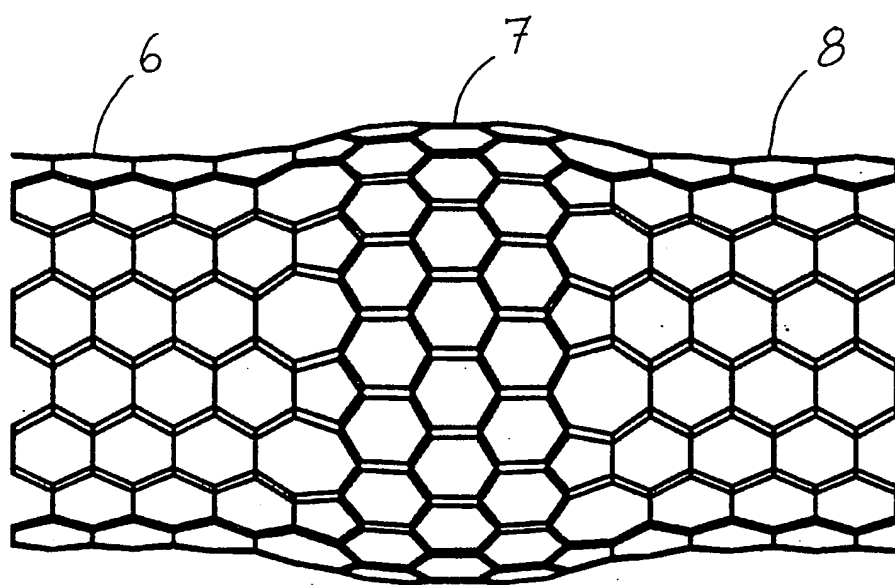


FIG. 2

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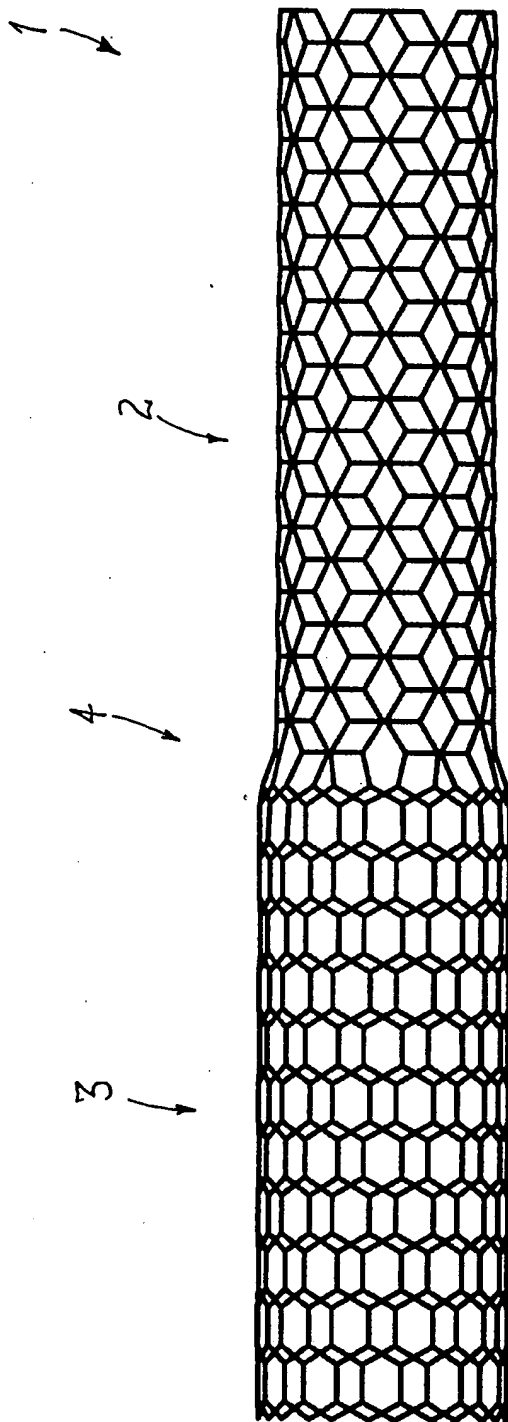


FIG. 1

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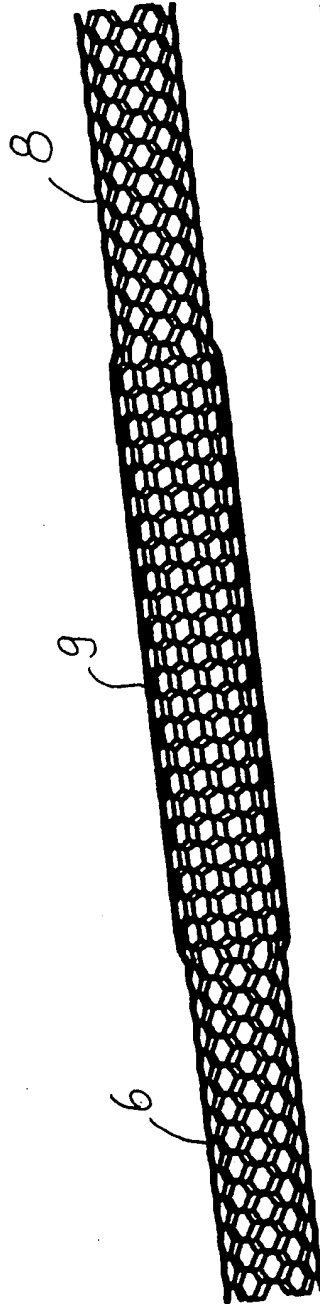


FIG. 3

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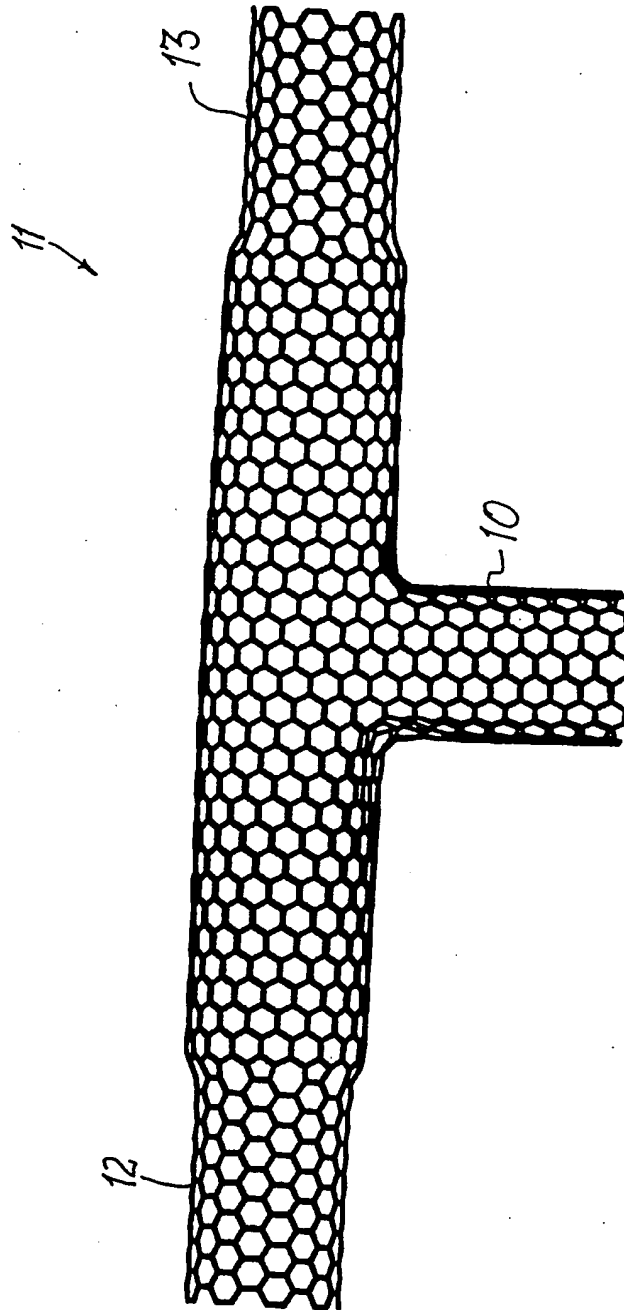


FIG. 4

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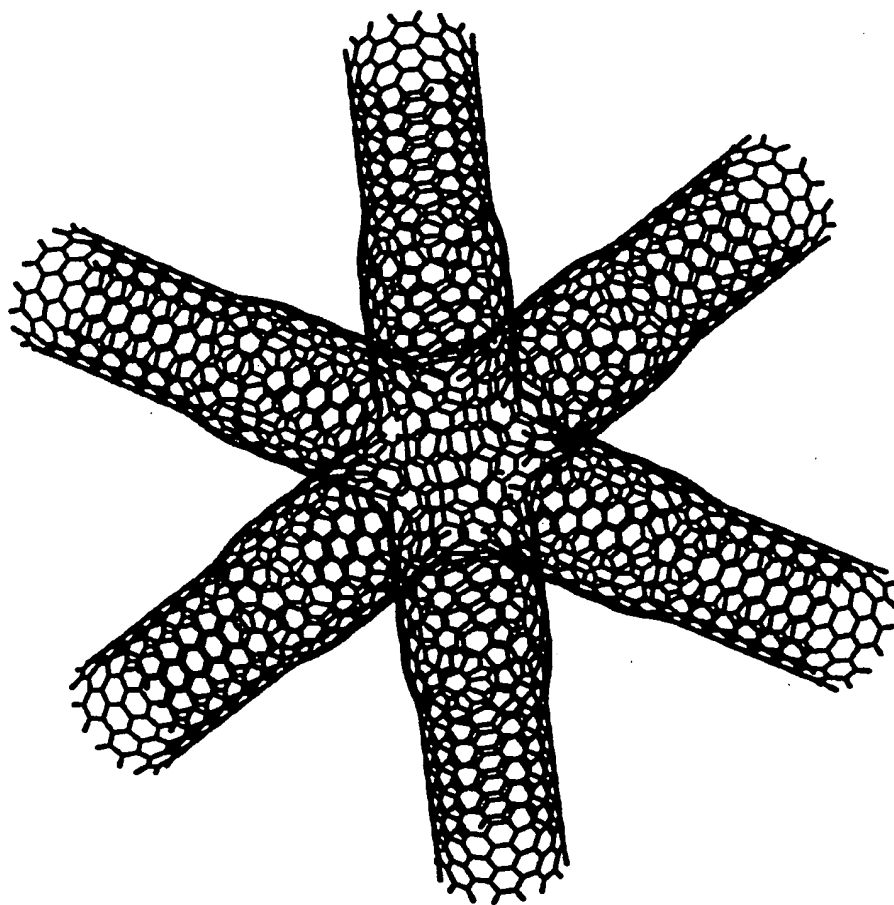


FIG. 5

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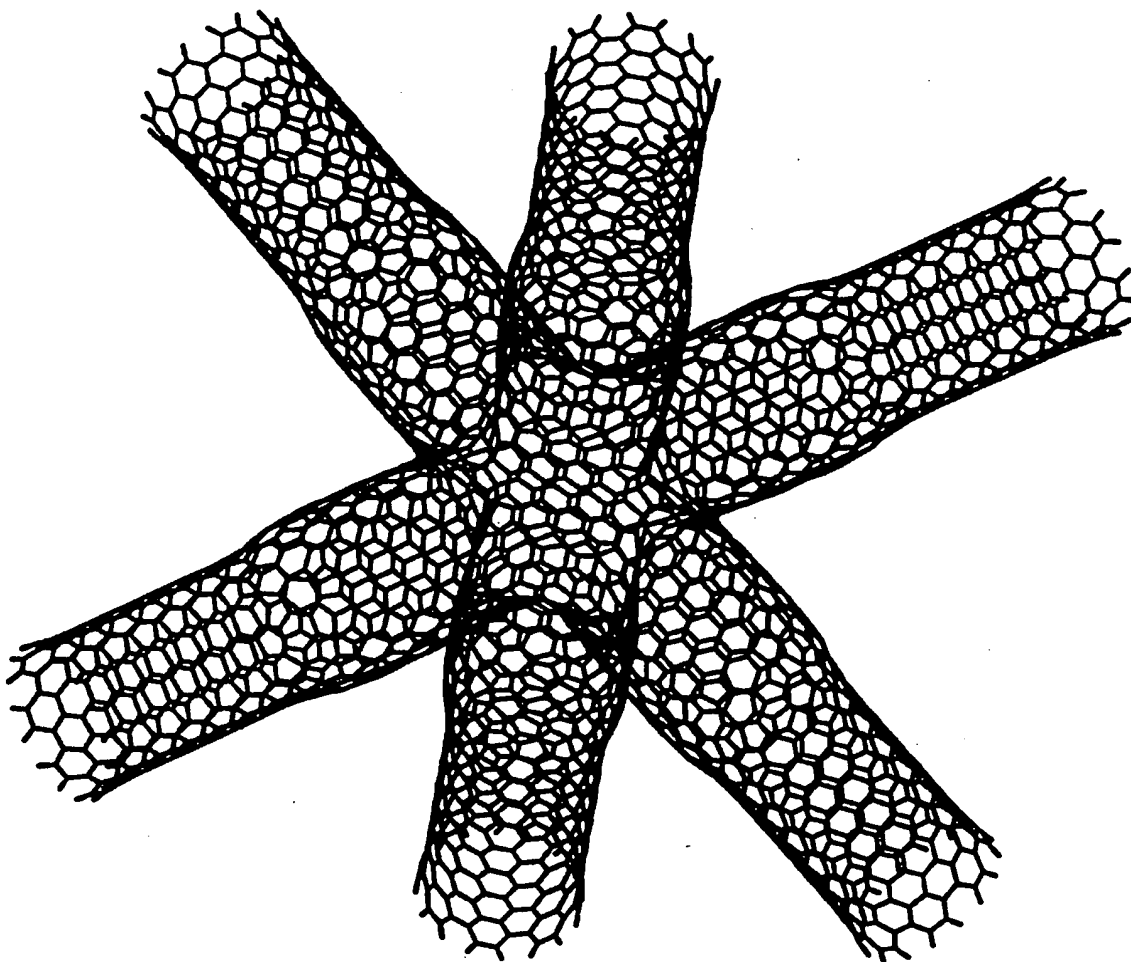
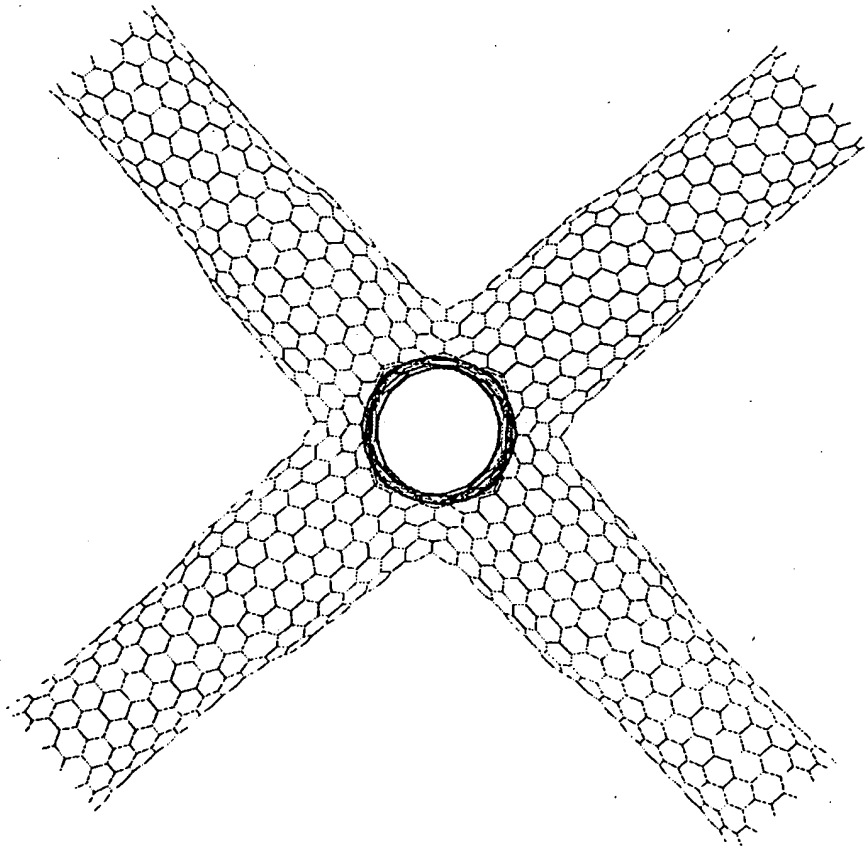


FIG. 6

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FIG. 7



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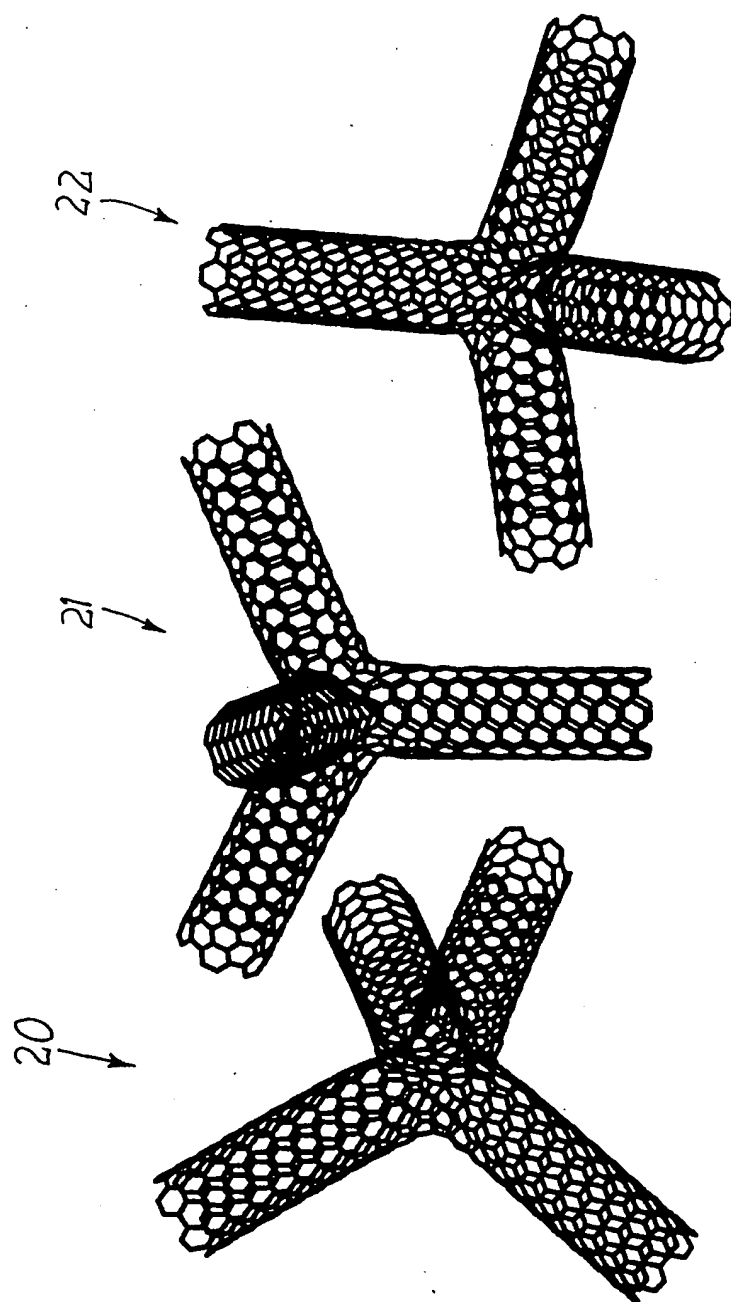


FIG. 8

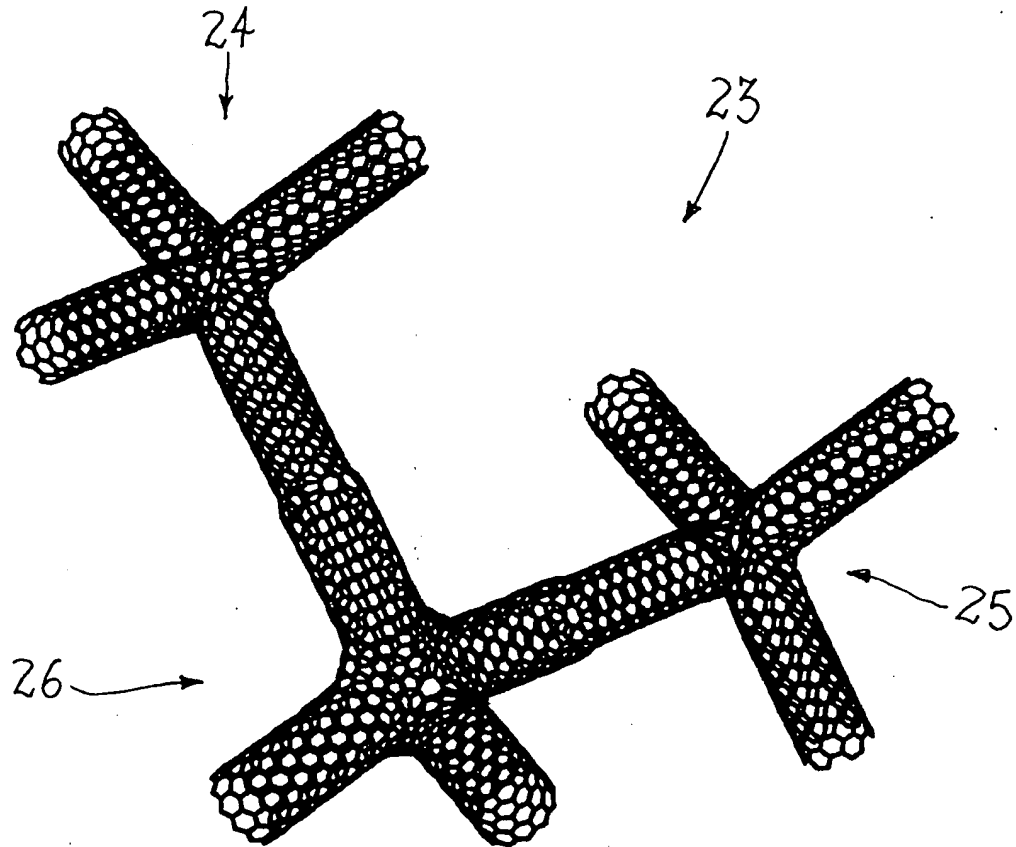


FIG. 9

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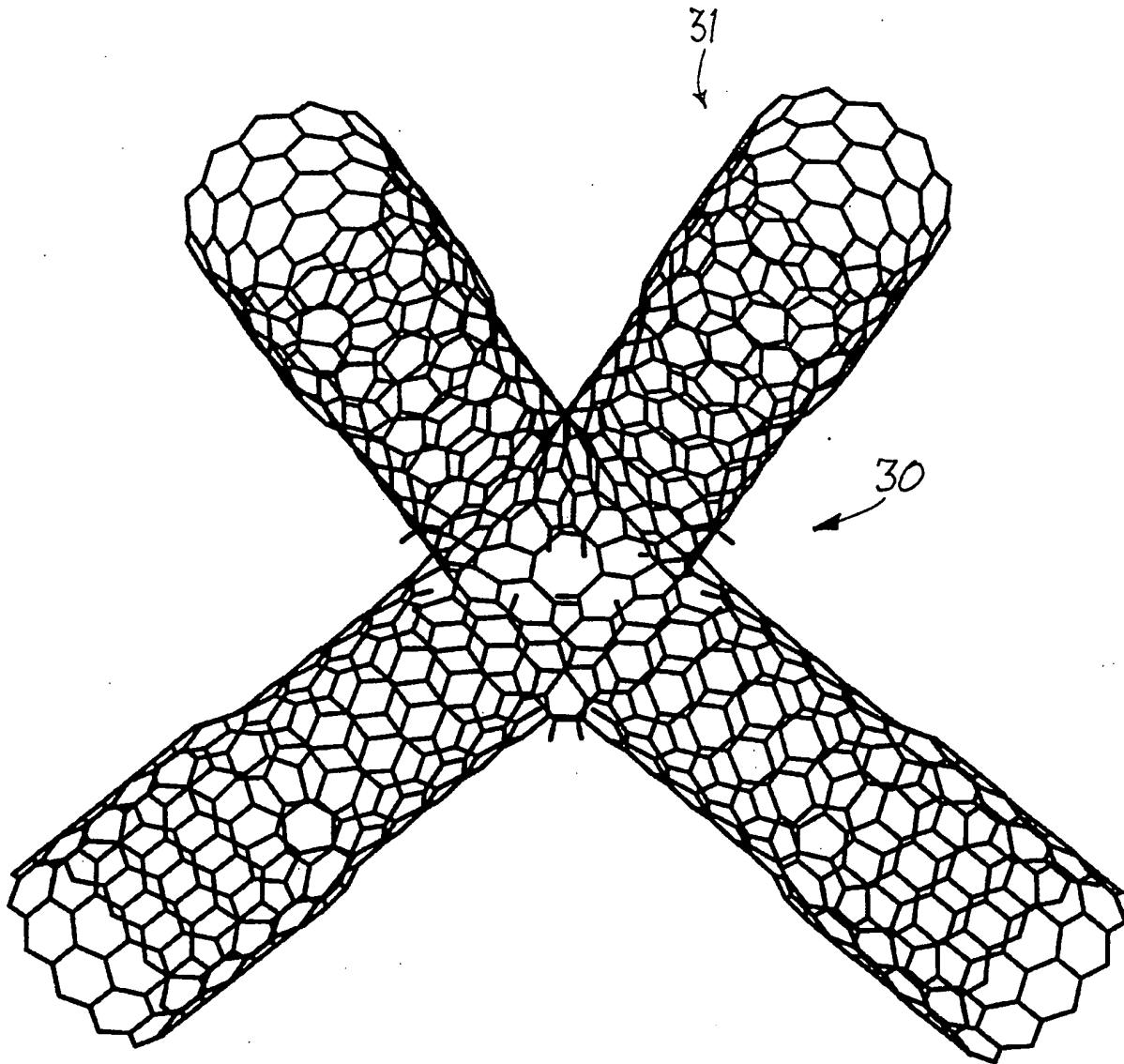


FIG. 10

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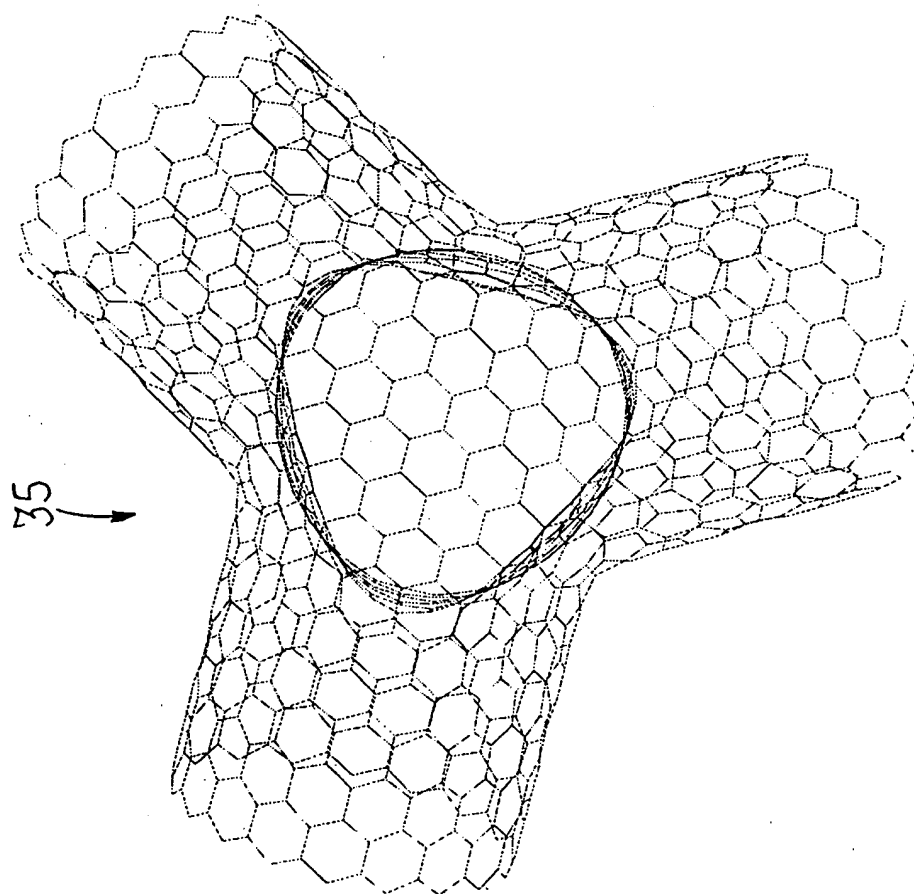
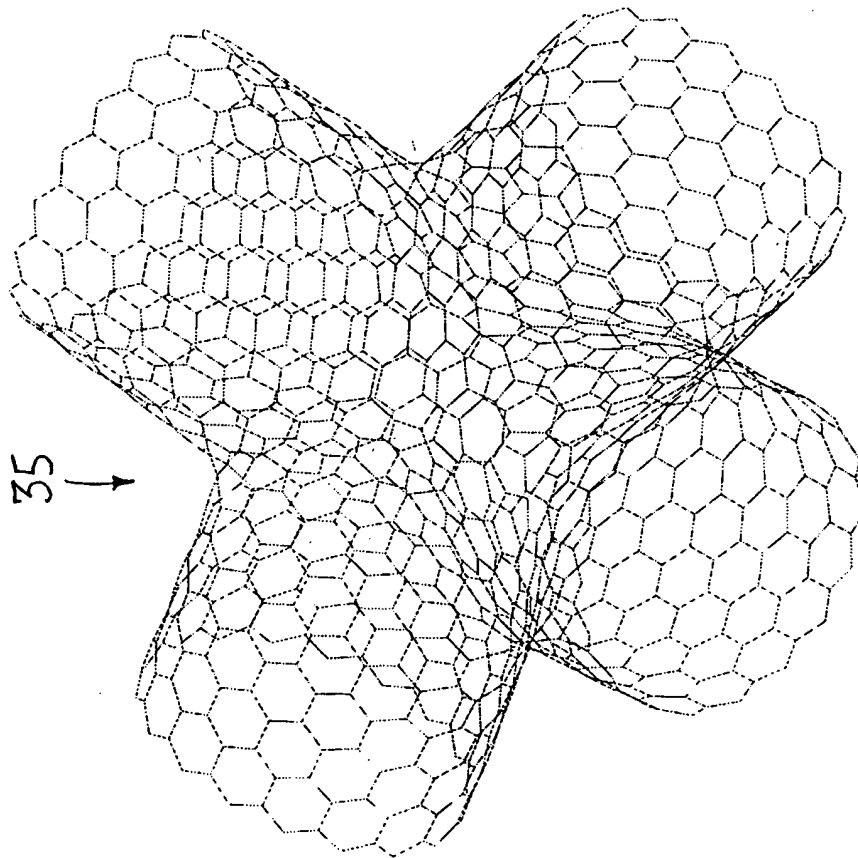


FIG. 11

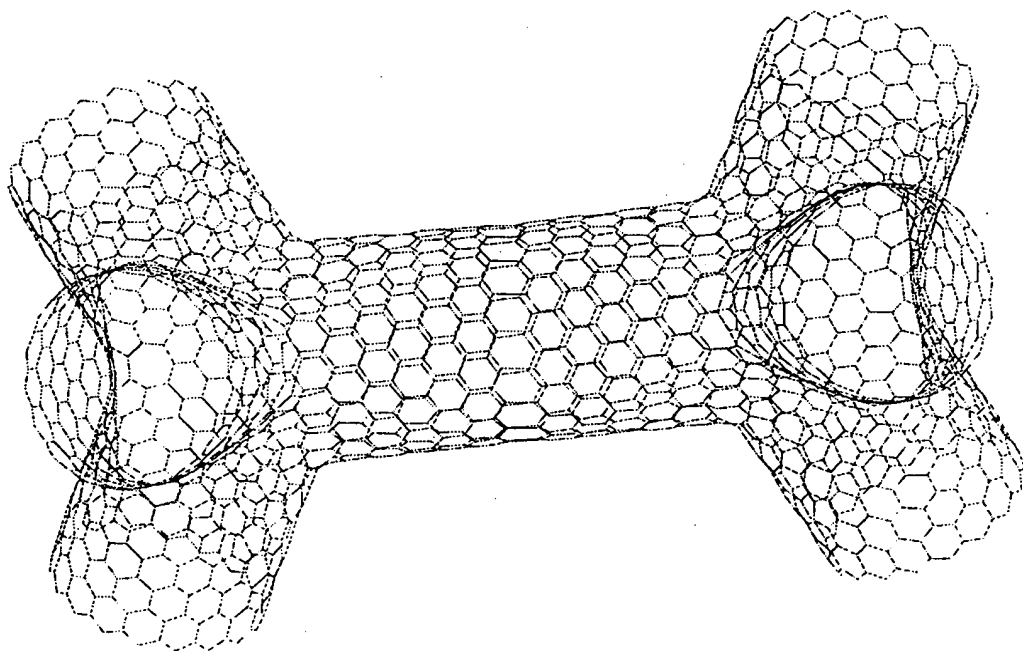
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FIG. 12



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FIG. 13



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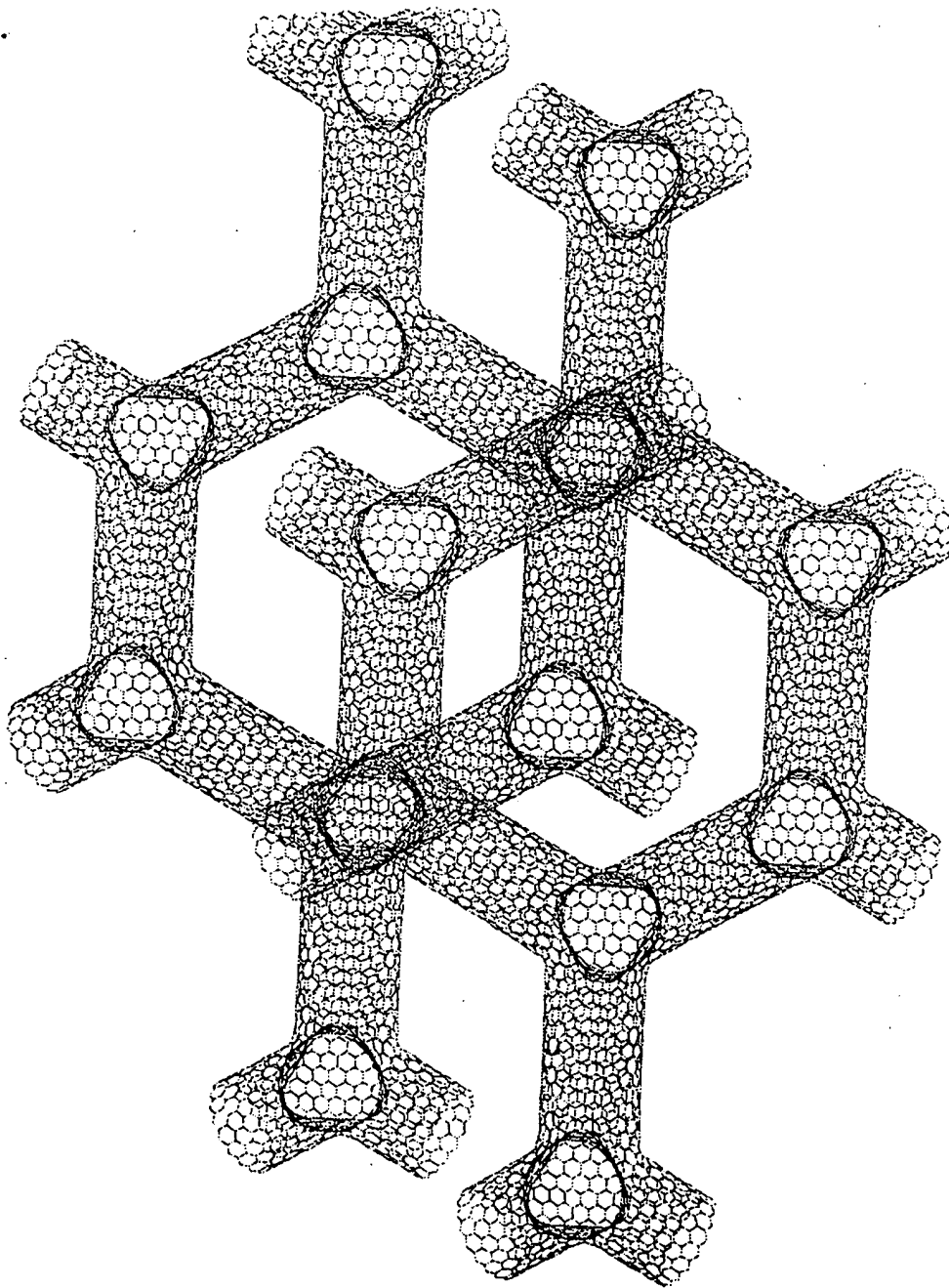


FIG. 14

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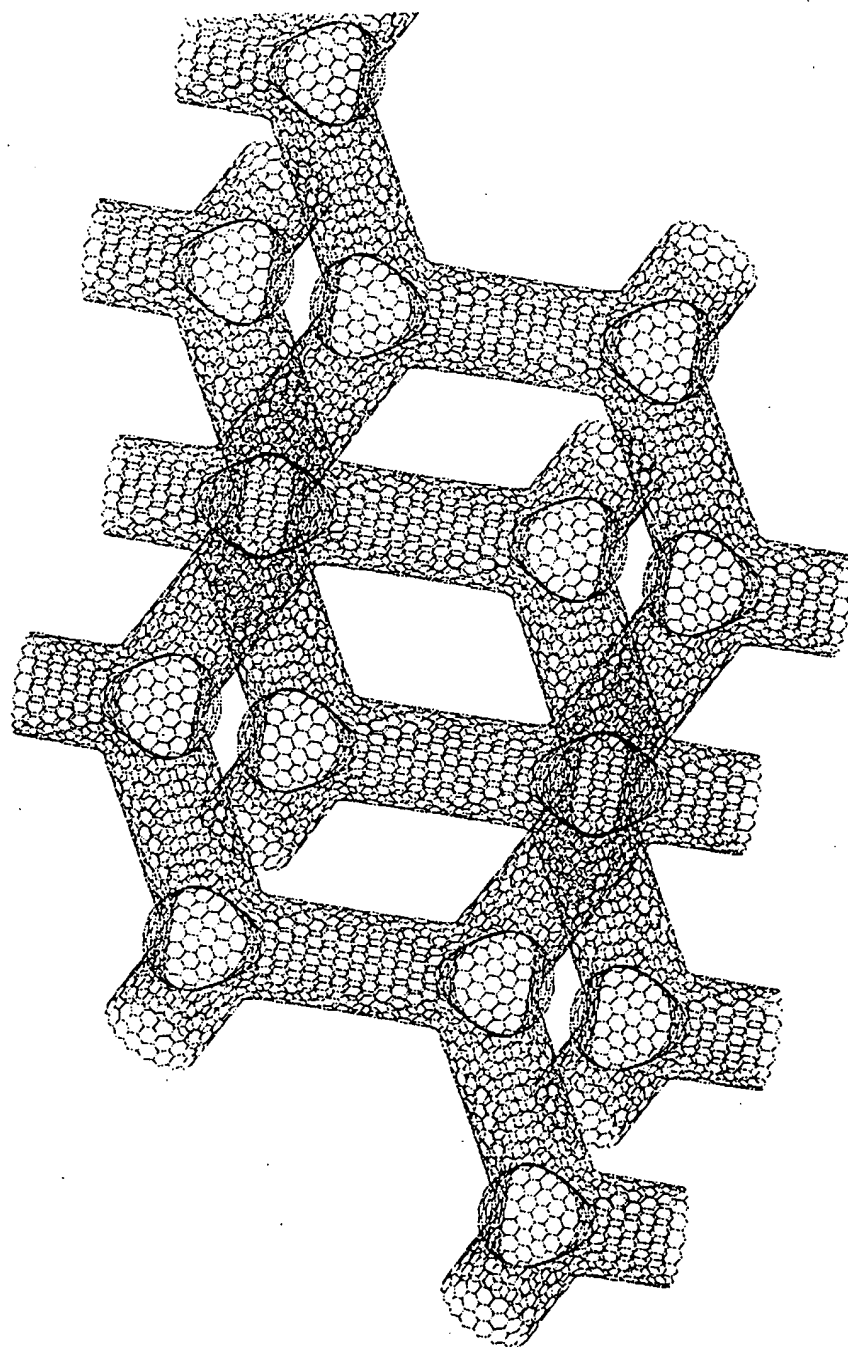


FIG. 15

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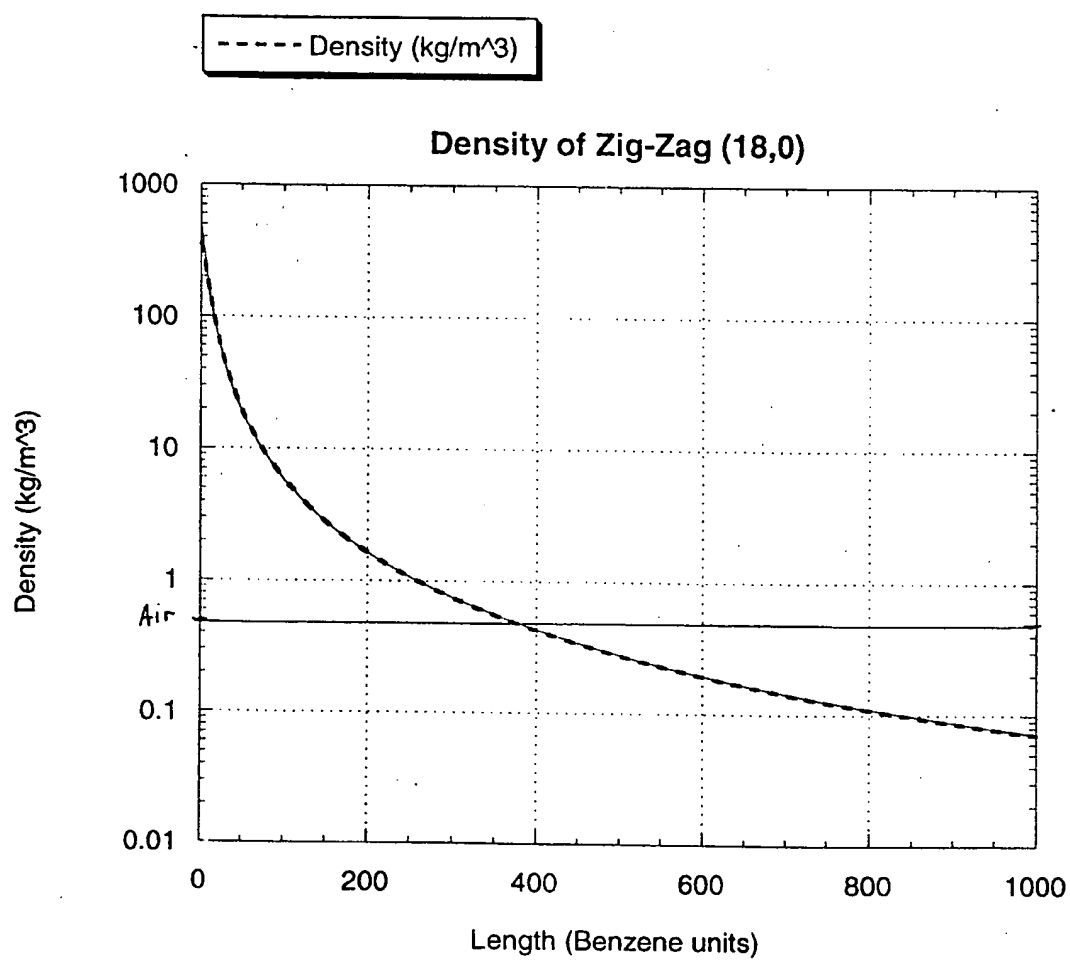


FIG. 16

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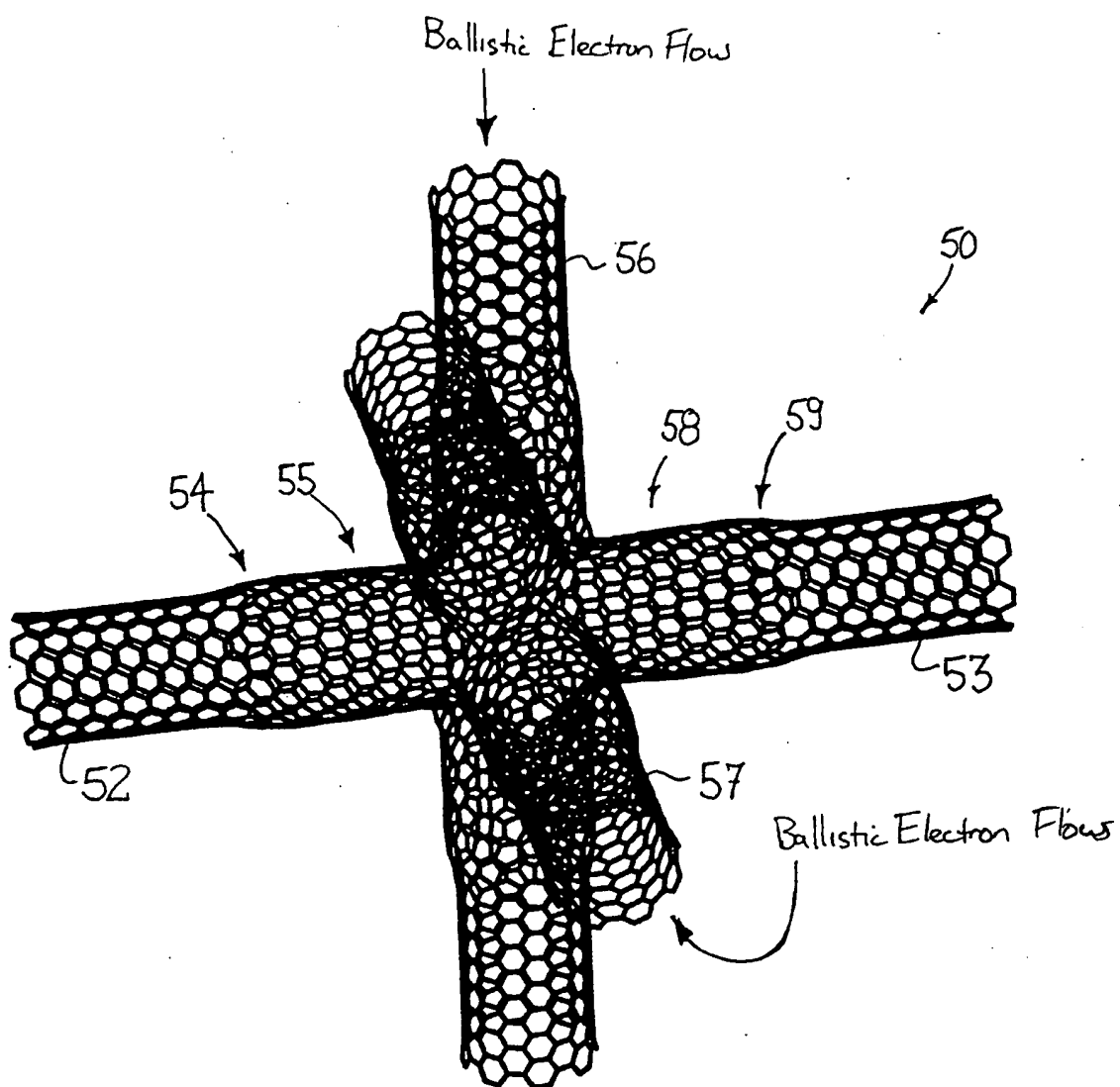


FIG. 17

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Zigzag precursor synthesis

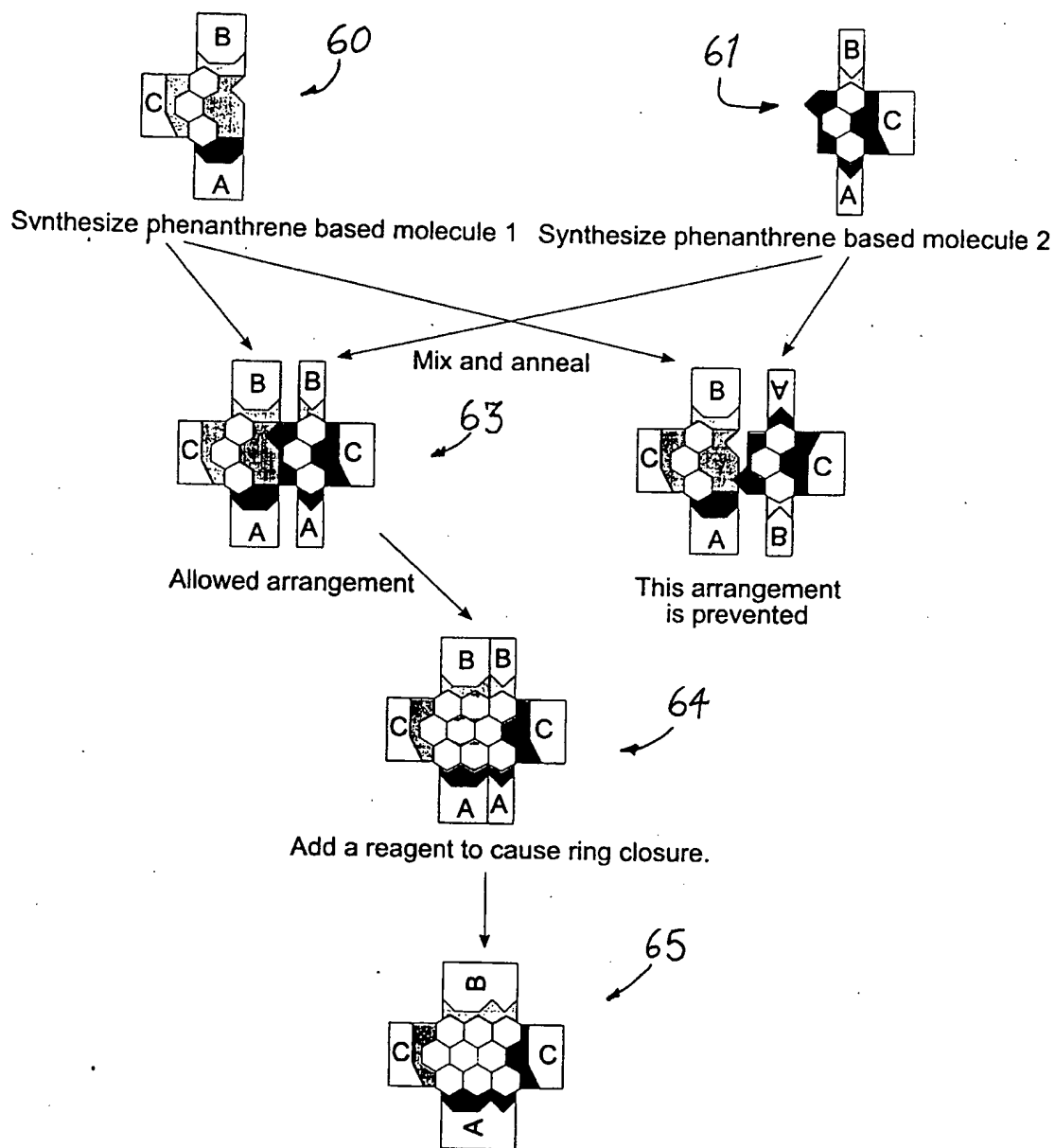


FIG. 18

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Armchair (8,8) precursor synthesis

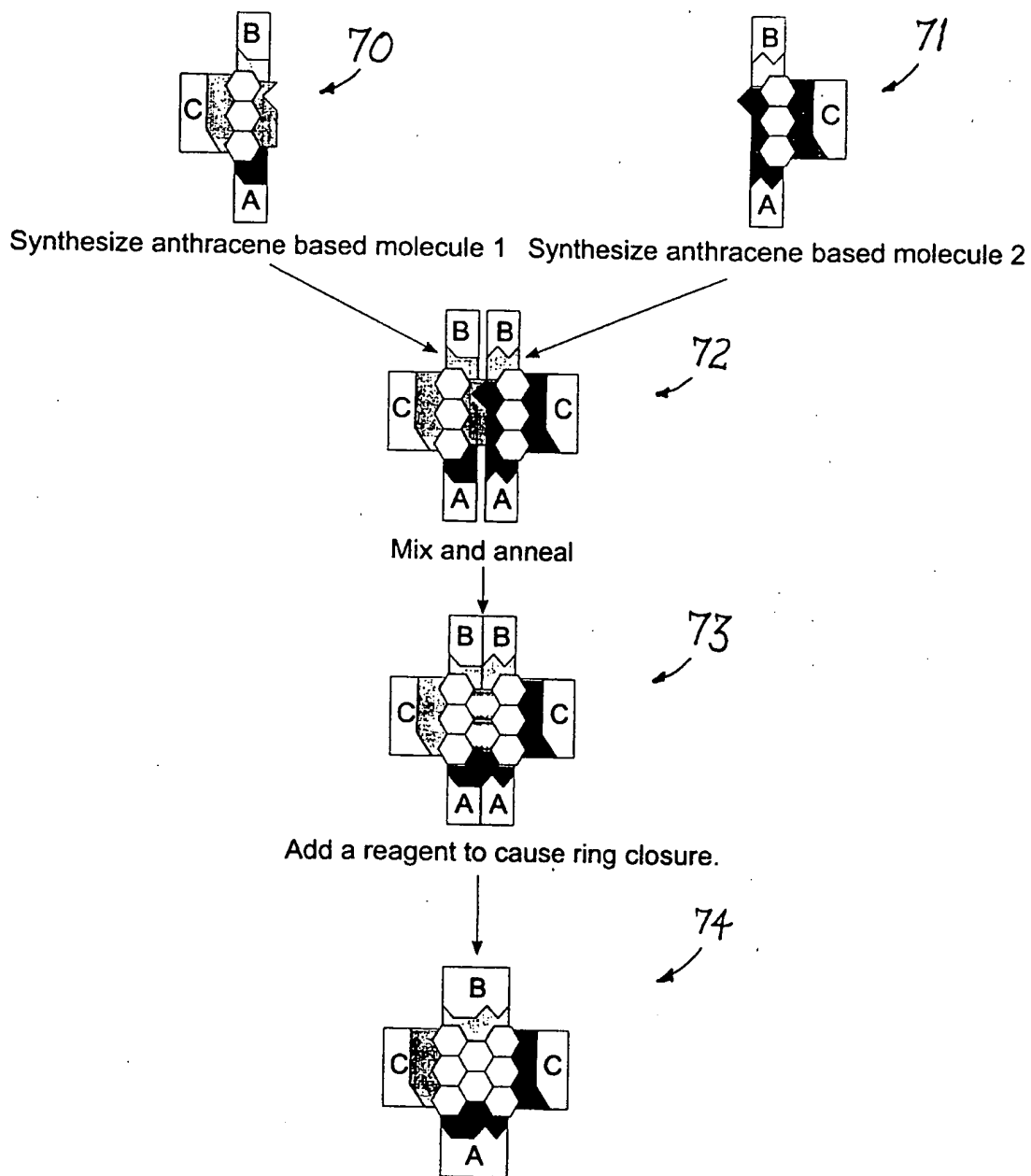


FIG. 19

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Double-ended zigzag (16,0) precursor synthesis

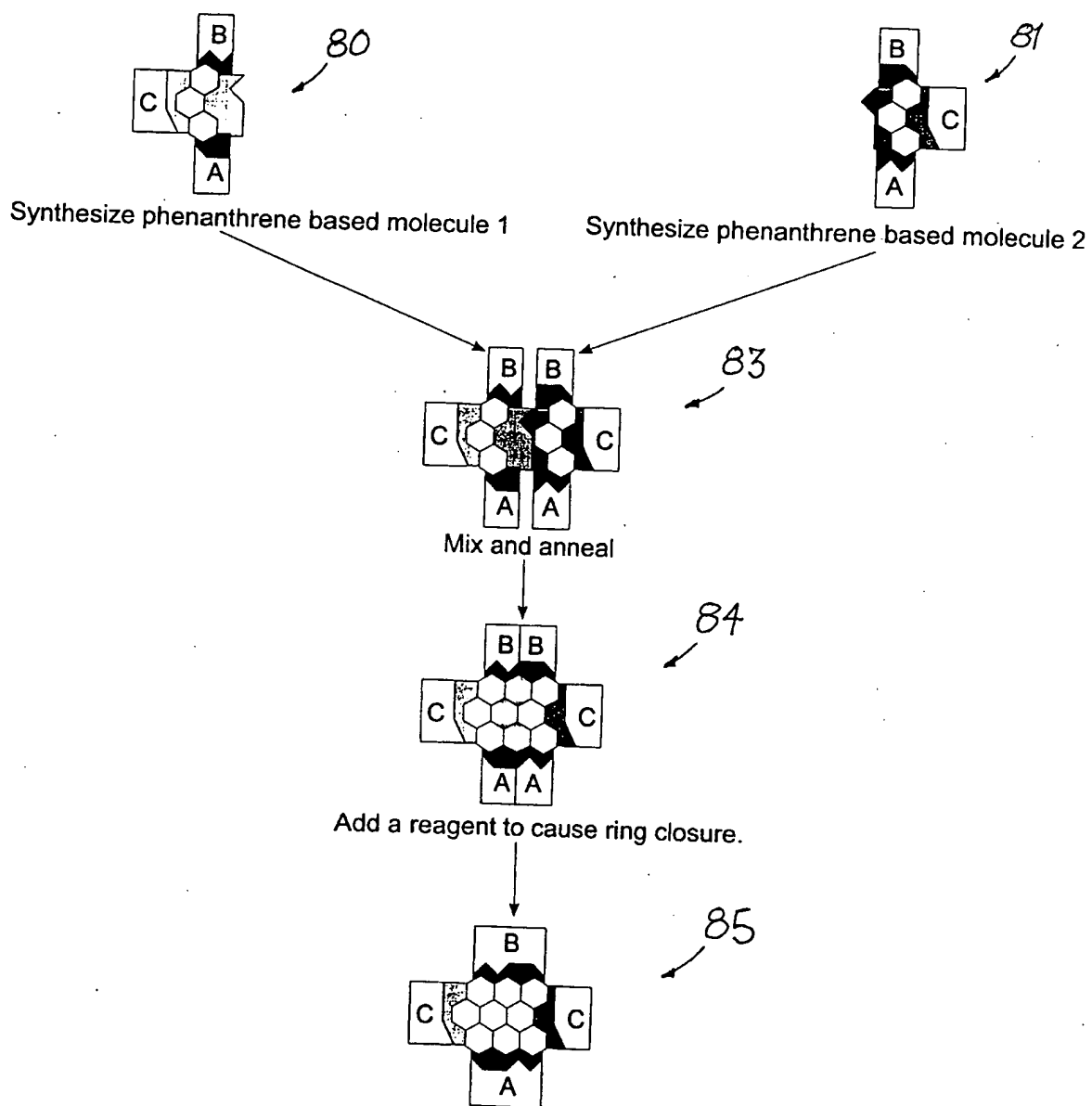
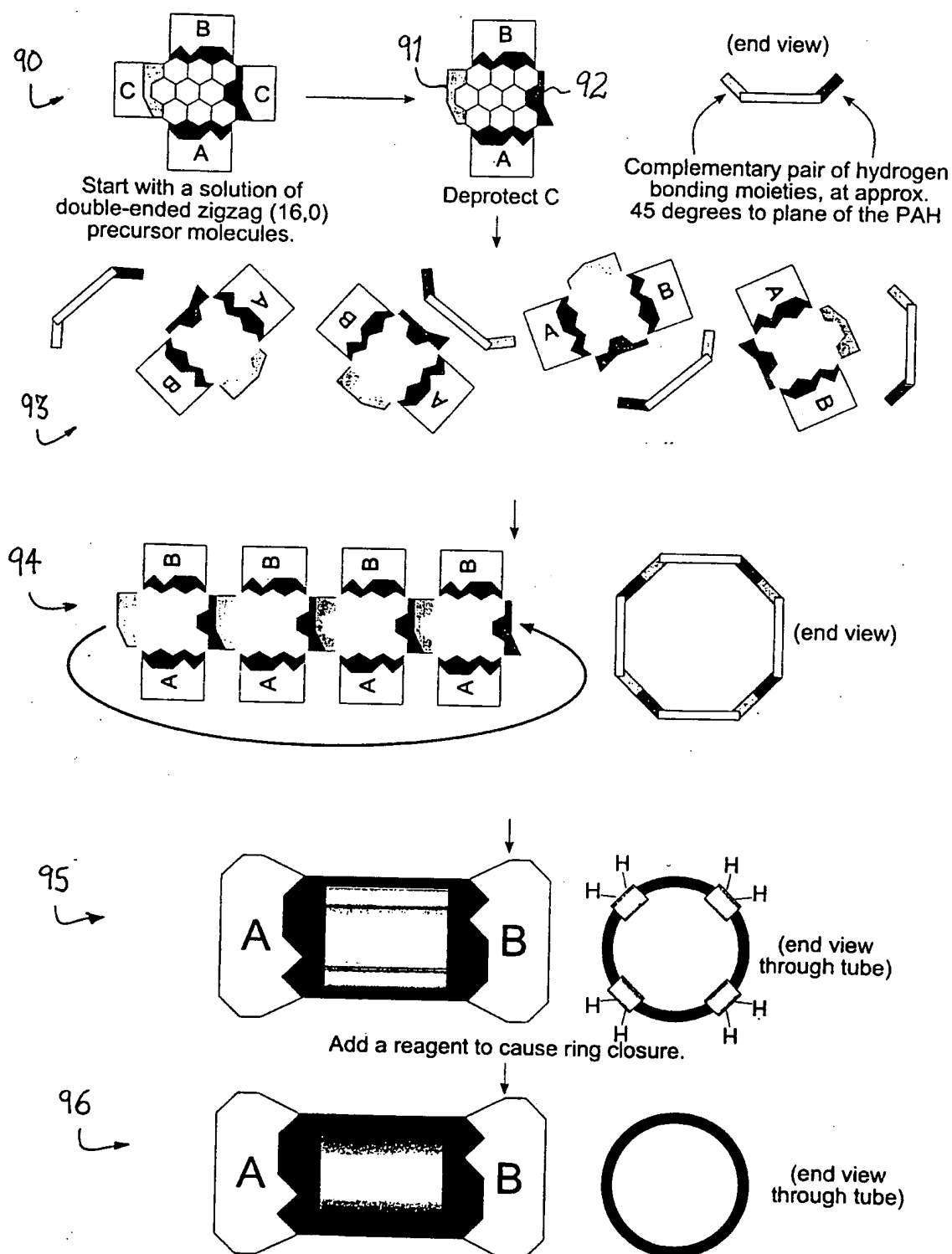


FIG. 20

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Double ended zigzag (16,0) nanotube synthesis



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Zigzag (16,0) nanotube synthesis

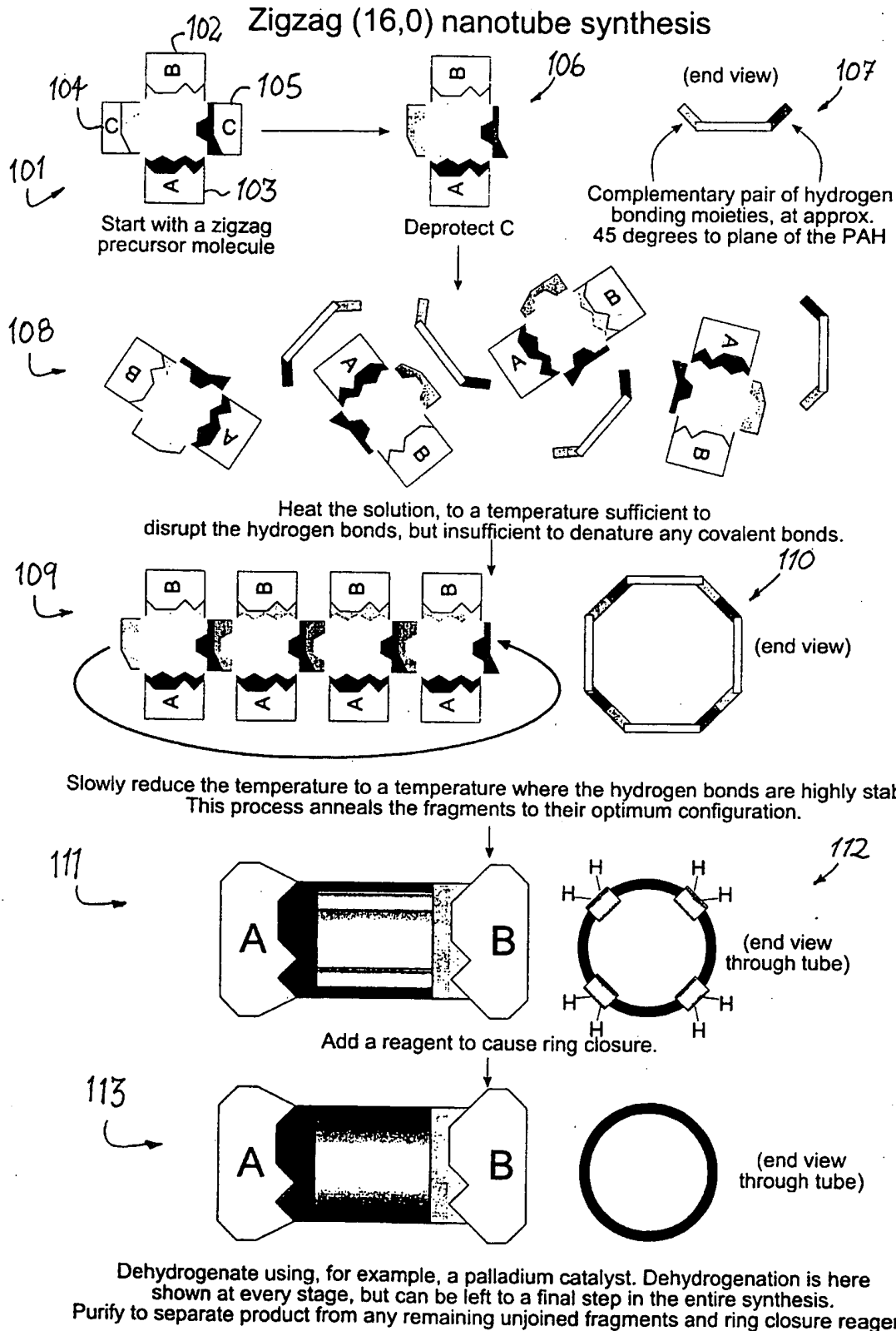


FIG. 22

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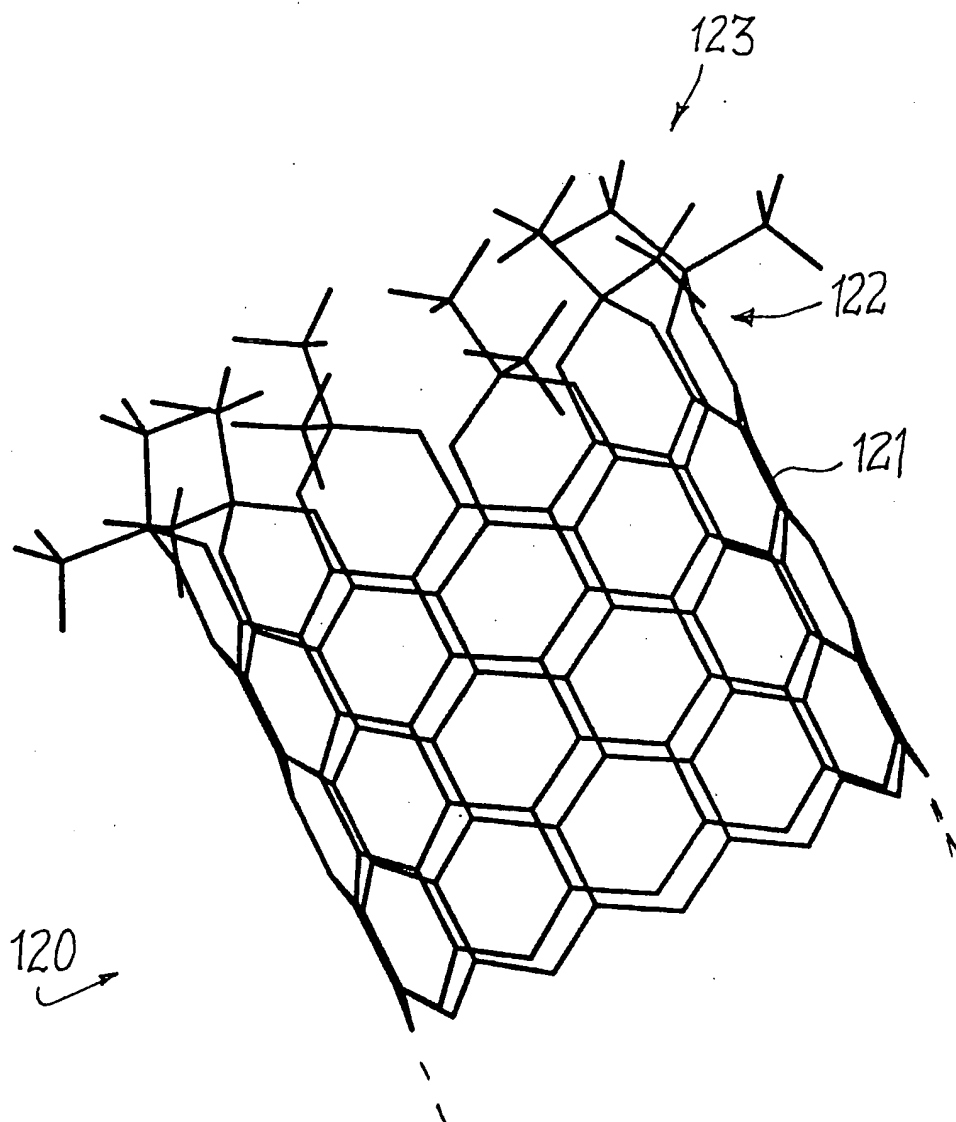
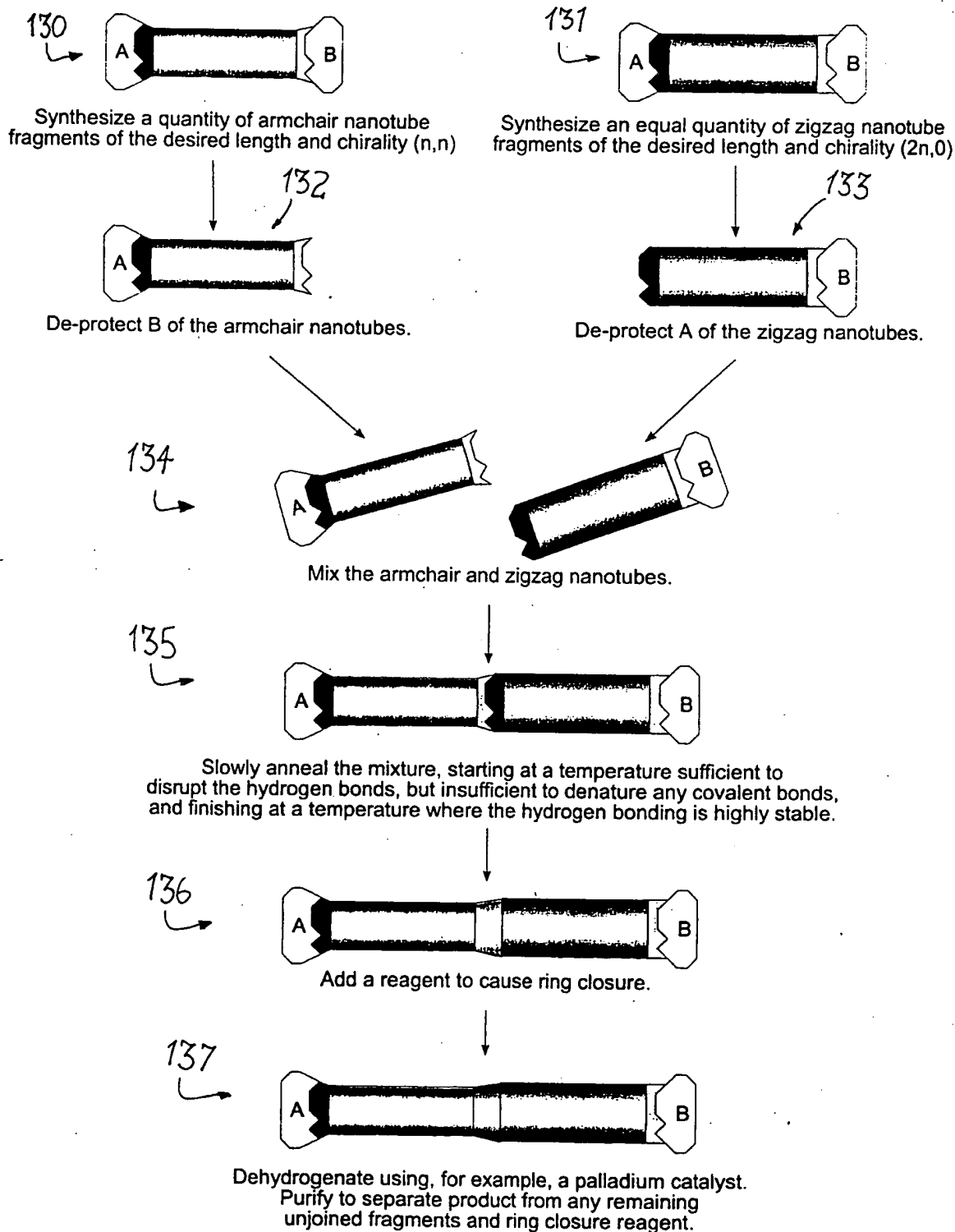


FIG. 23

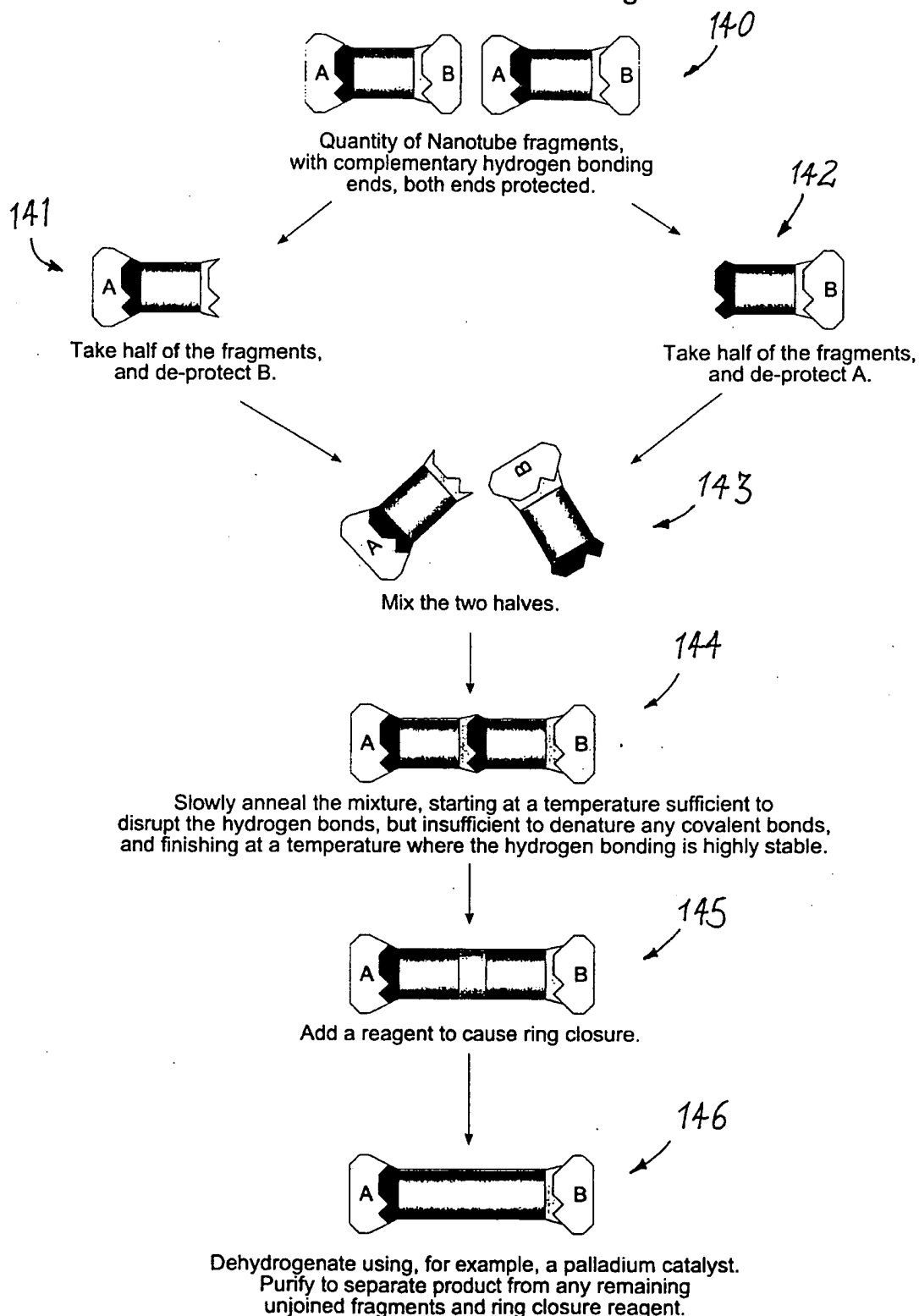
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Synthesis of nanotube linear diodes



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Controlled armchair nanotube length increase



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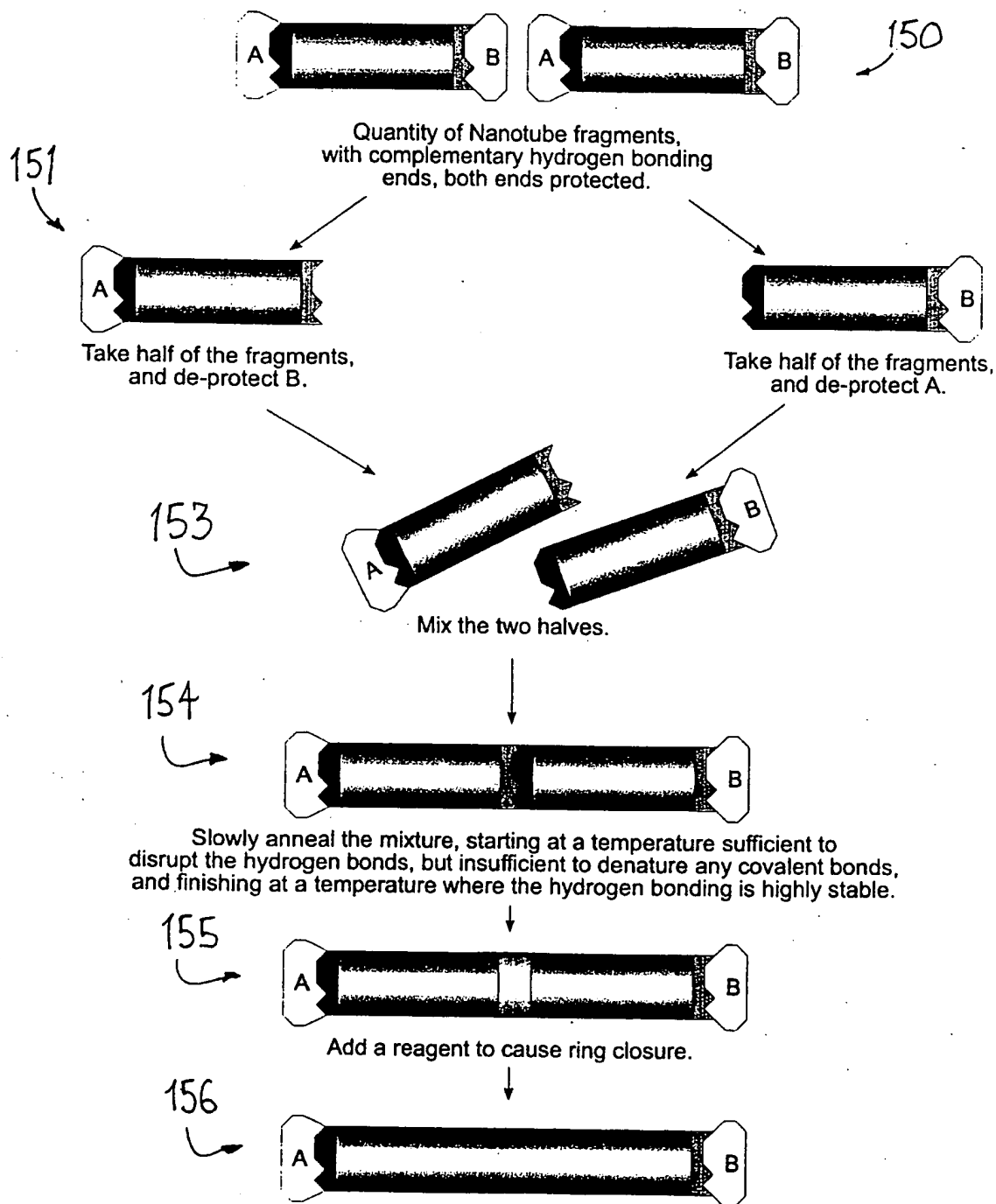


FIG. 26

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Synthesis of nanotube 'rods'

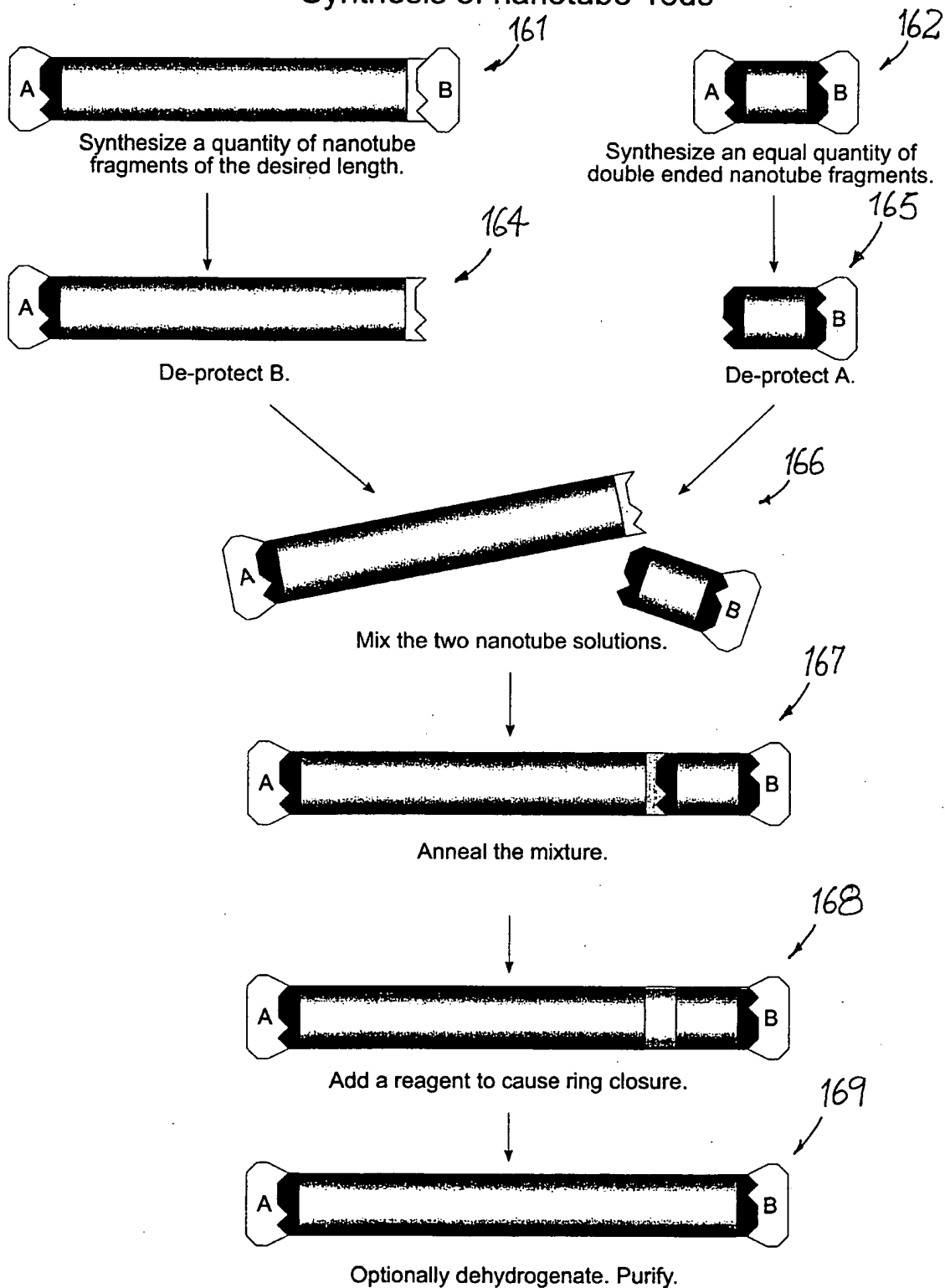
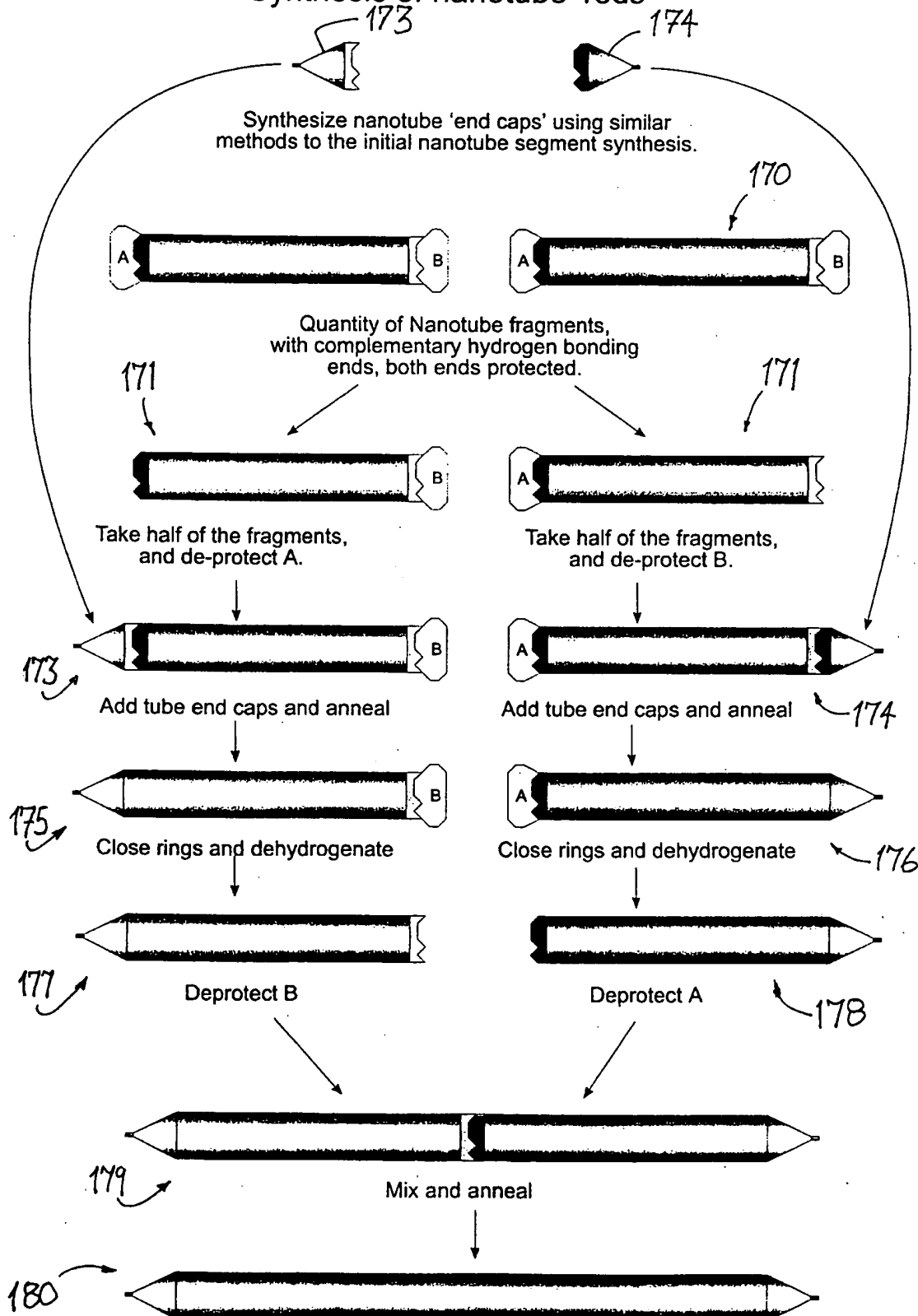


FIG. 27

SUBSTITUTE SHEET (Rule 26) (RO/AU)

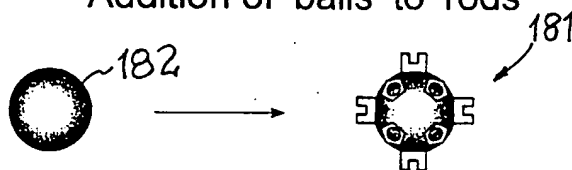
28 / 36

Synthesis of nanotube 'rods'

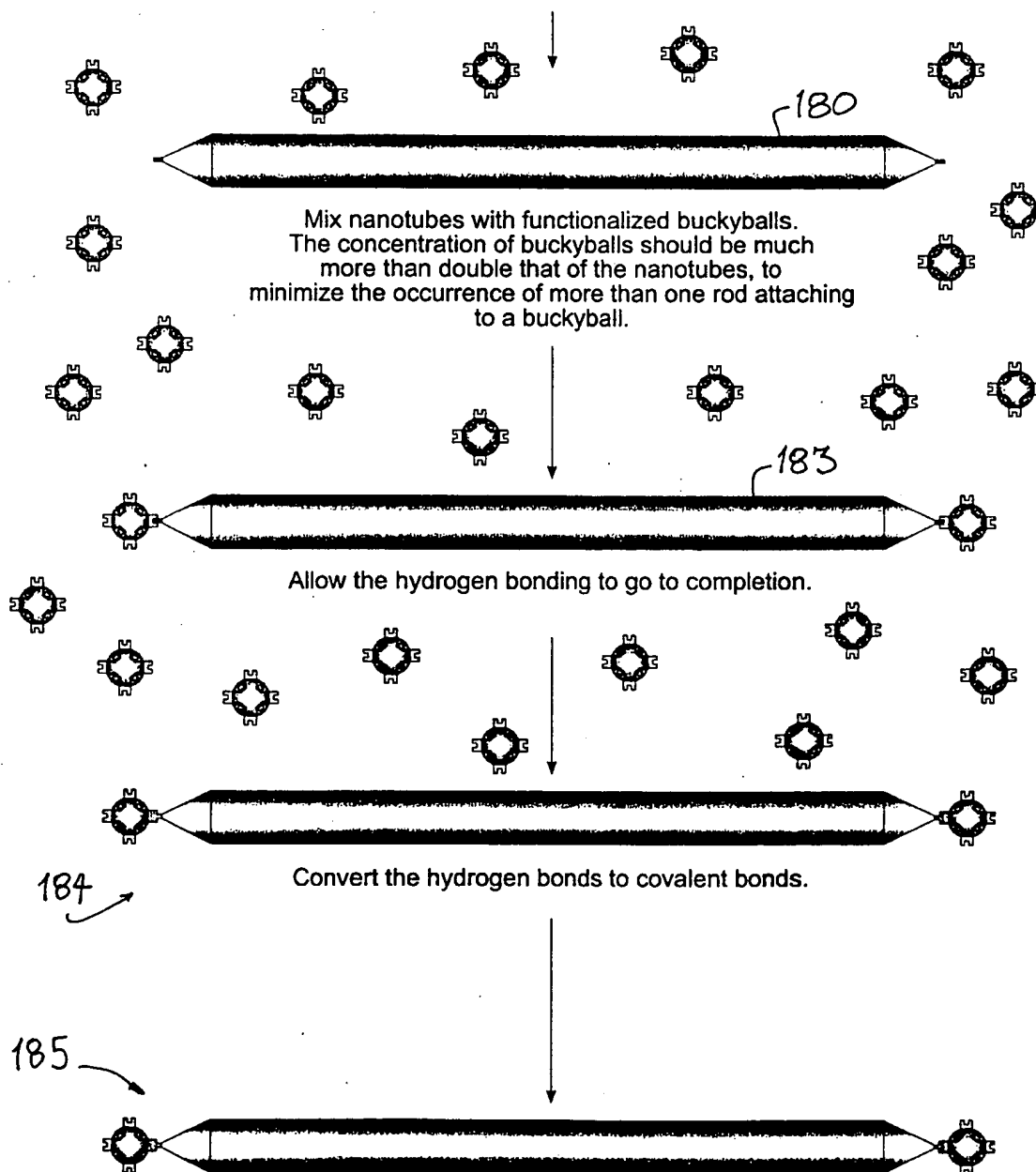


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Addition of 'balls' to 'rods'



Functionalize a Buckyball (C_{60} recommended due to high yield and purity) by attaching a hydrogen bonding moiety to each of the 12 five membered rings of the buckyball.



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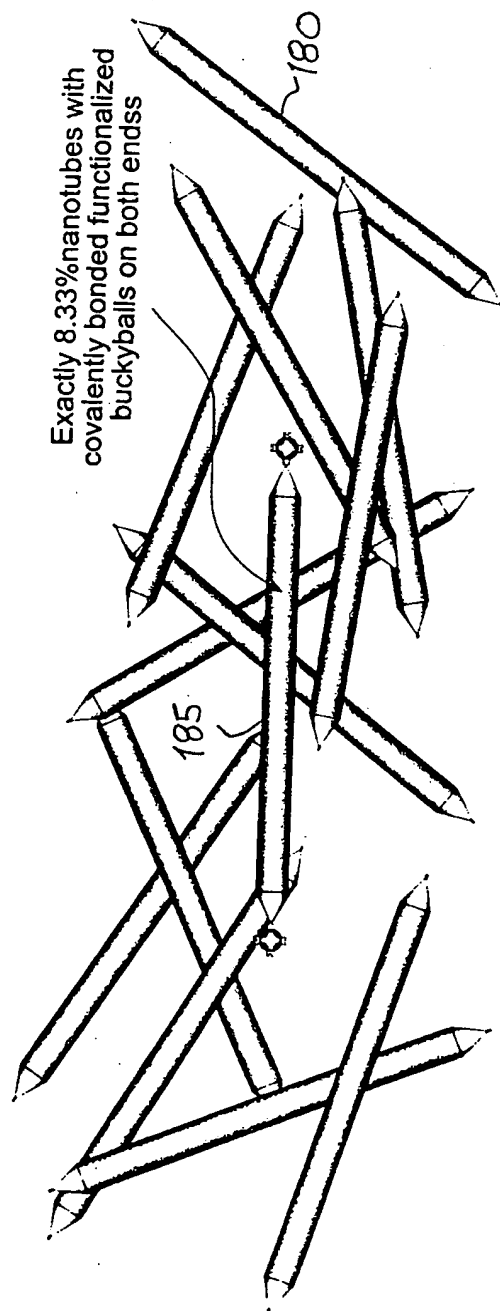
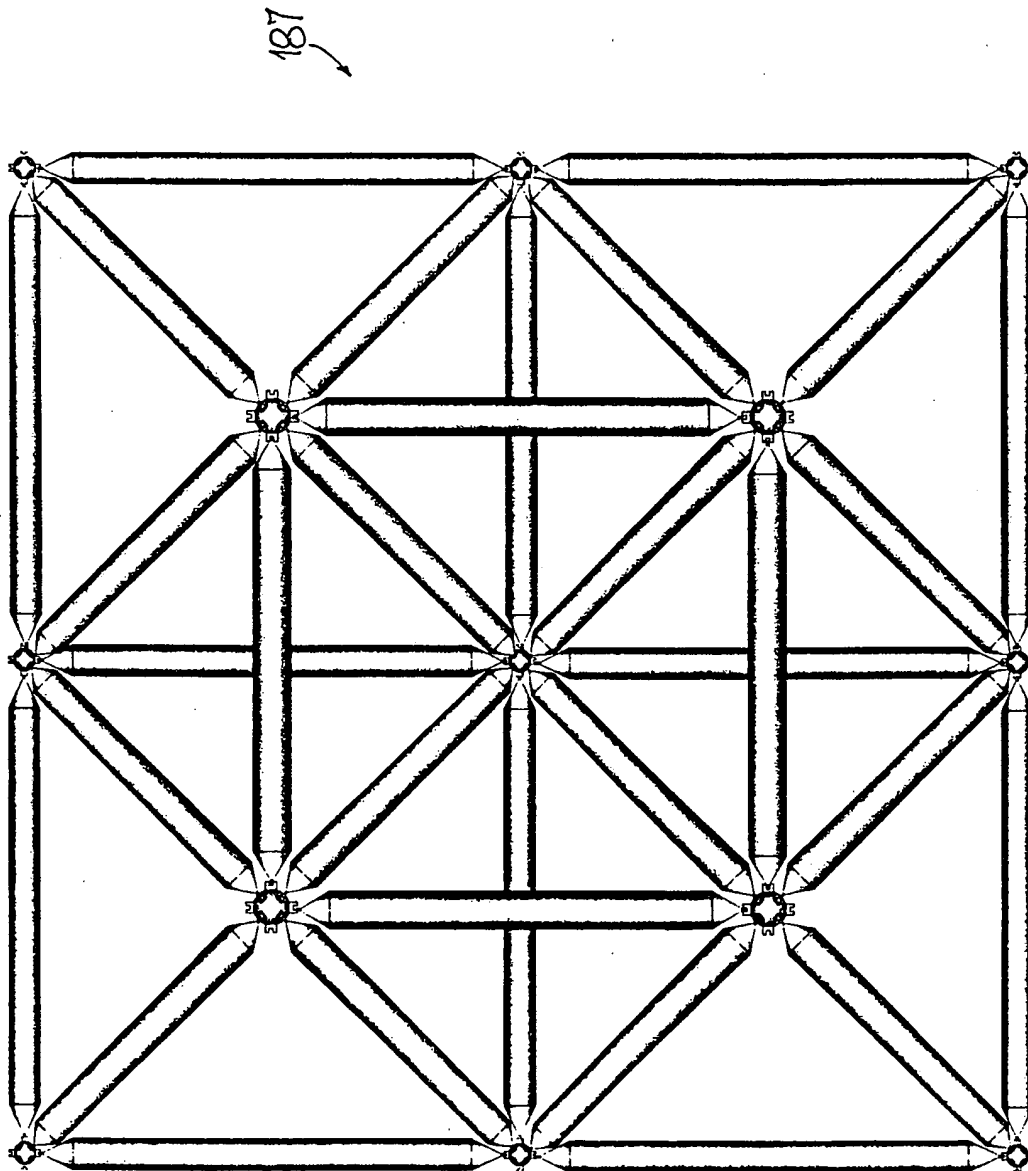


FIG. 30

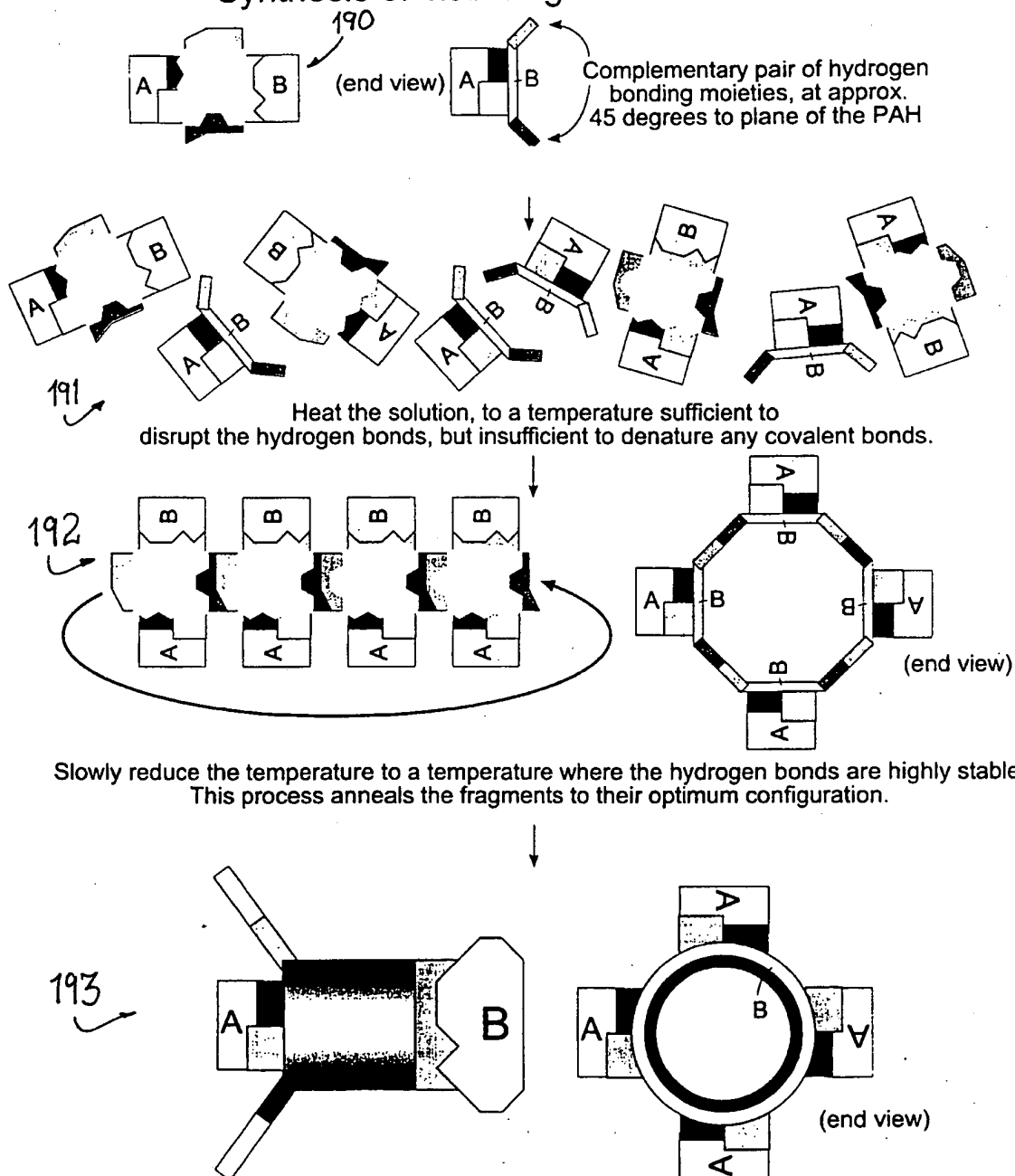
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FIG. 31



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Synthesis of 'hub' fragments



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 Synthesis of 'hubs'

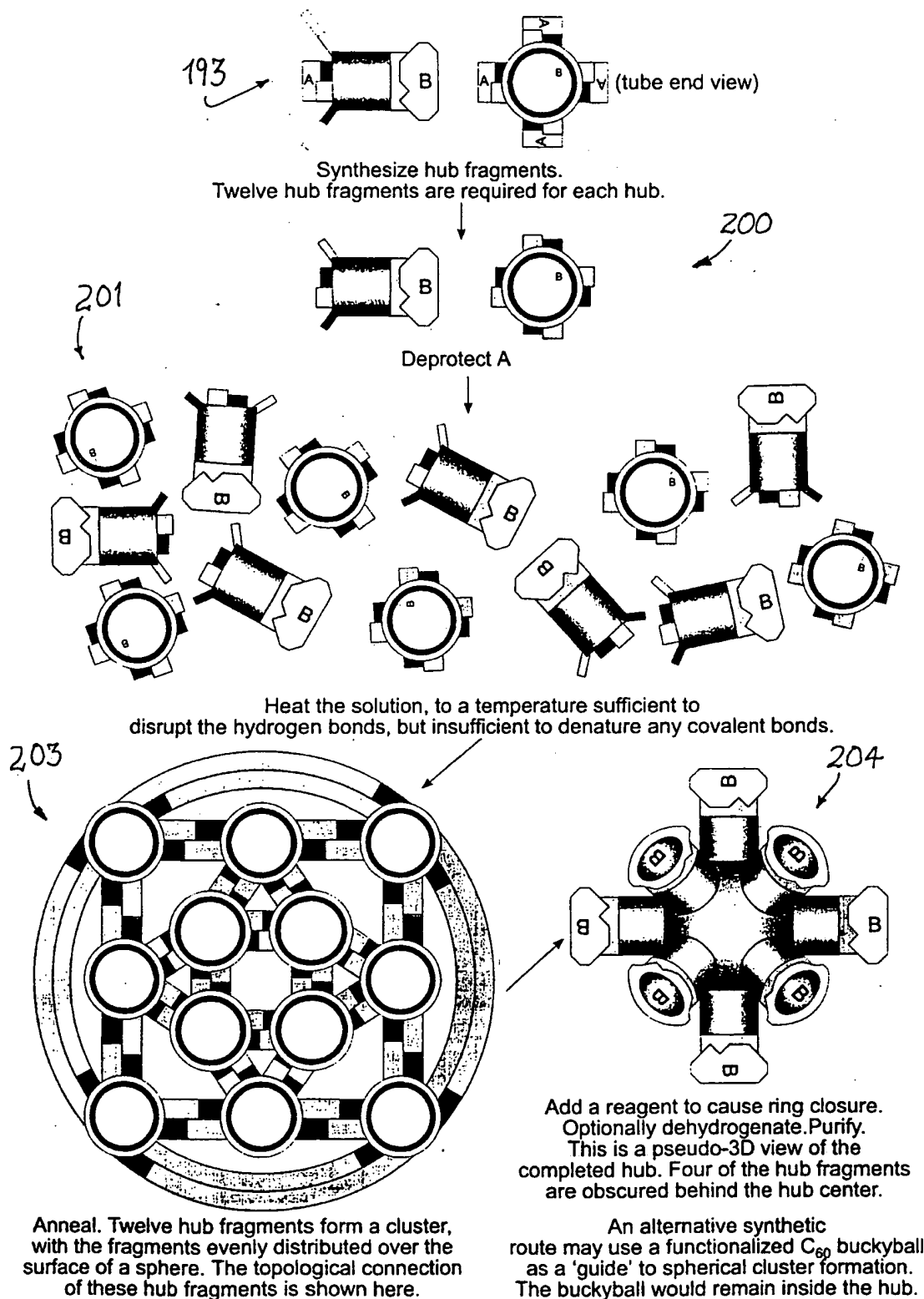
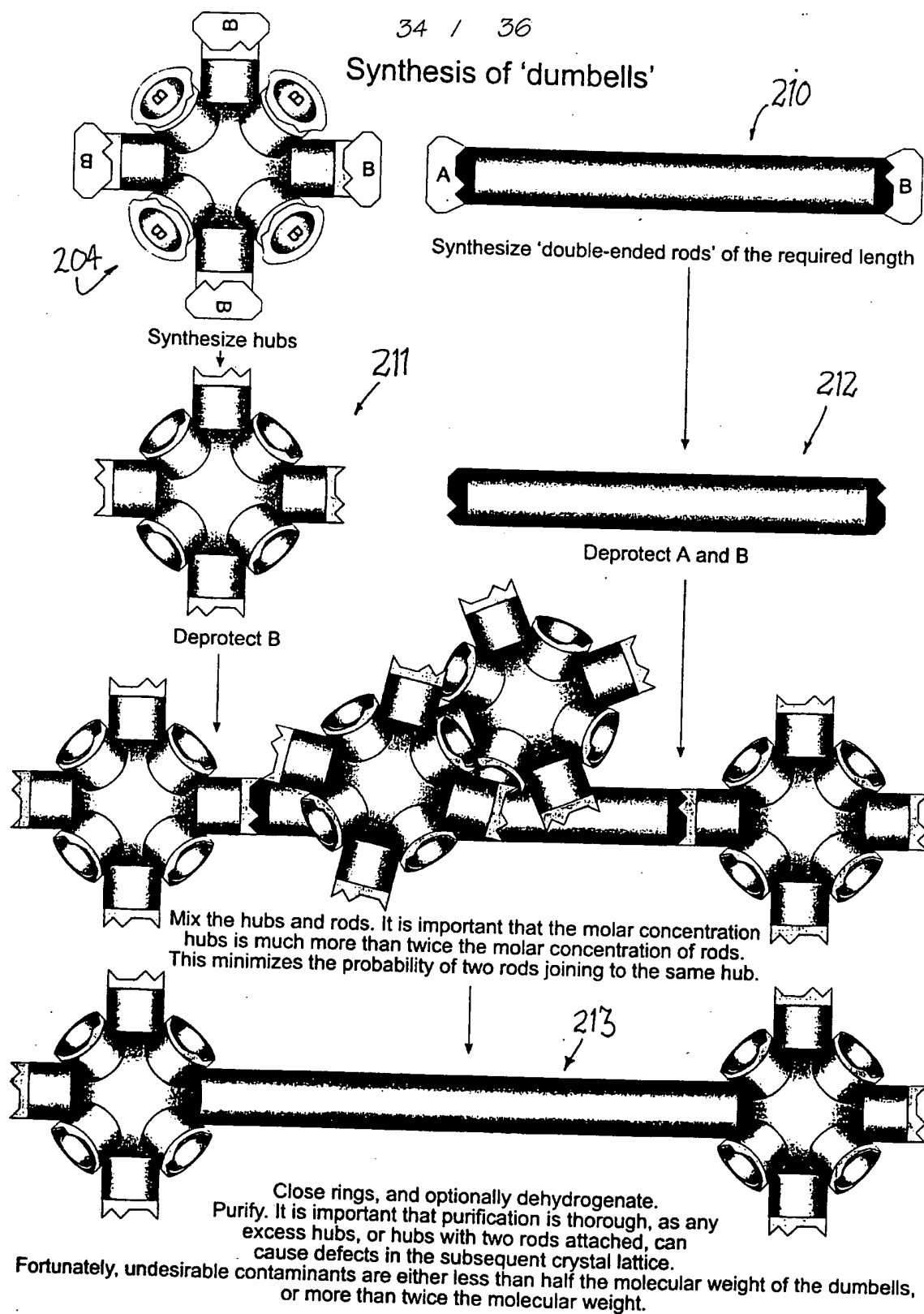


FIG. 33



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Synthesis of low density, high strength, nanotube crystals

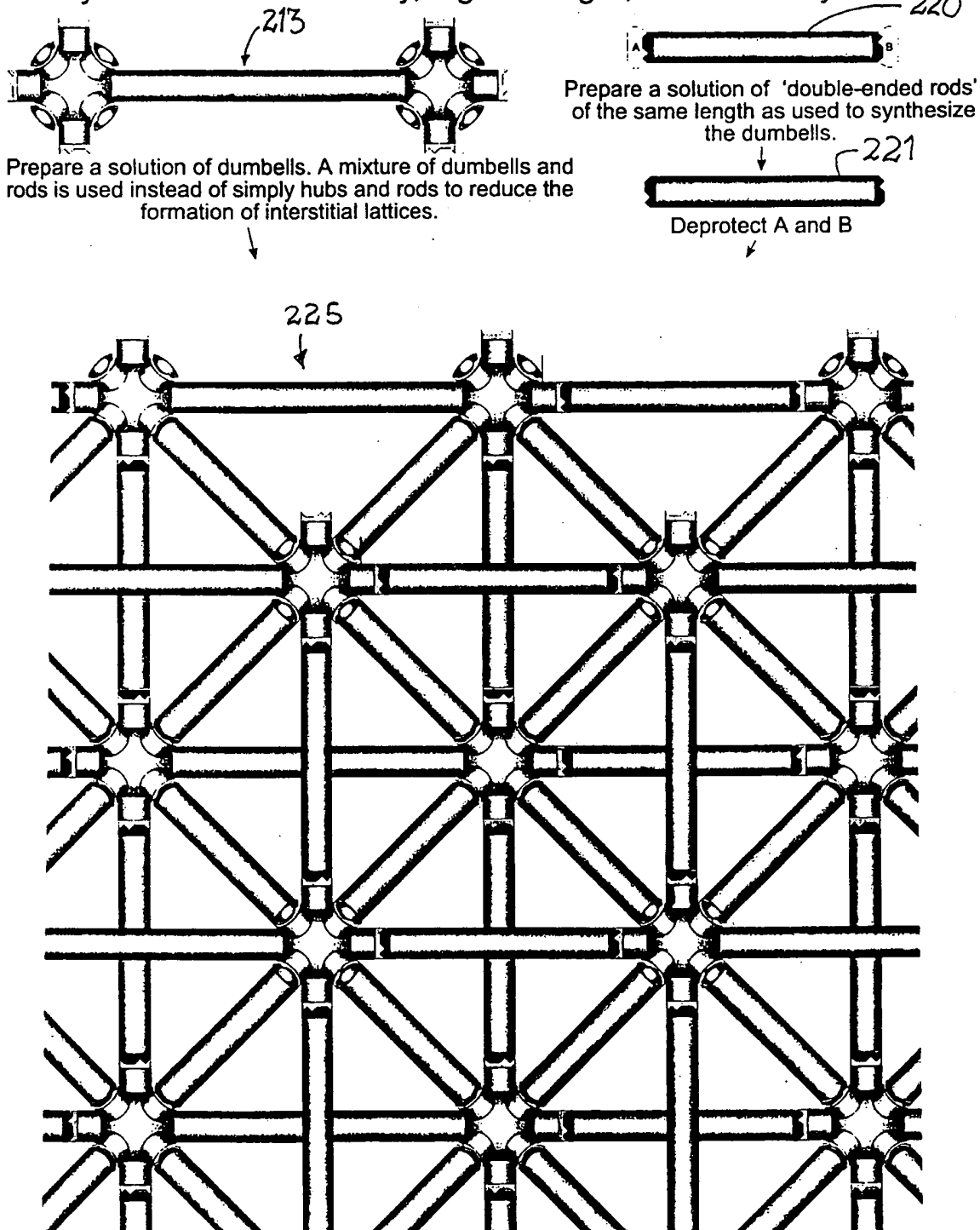


FIG. 35

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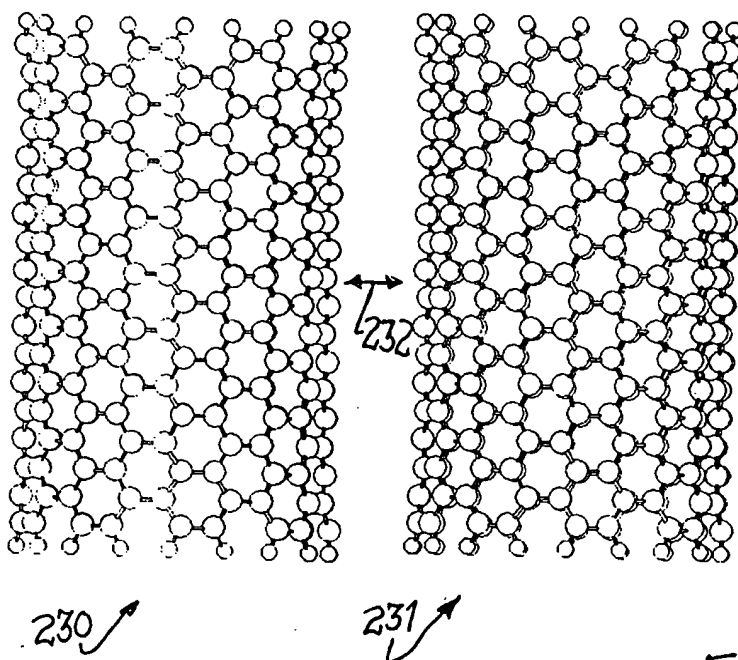
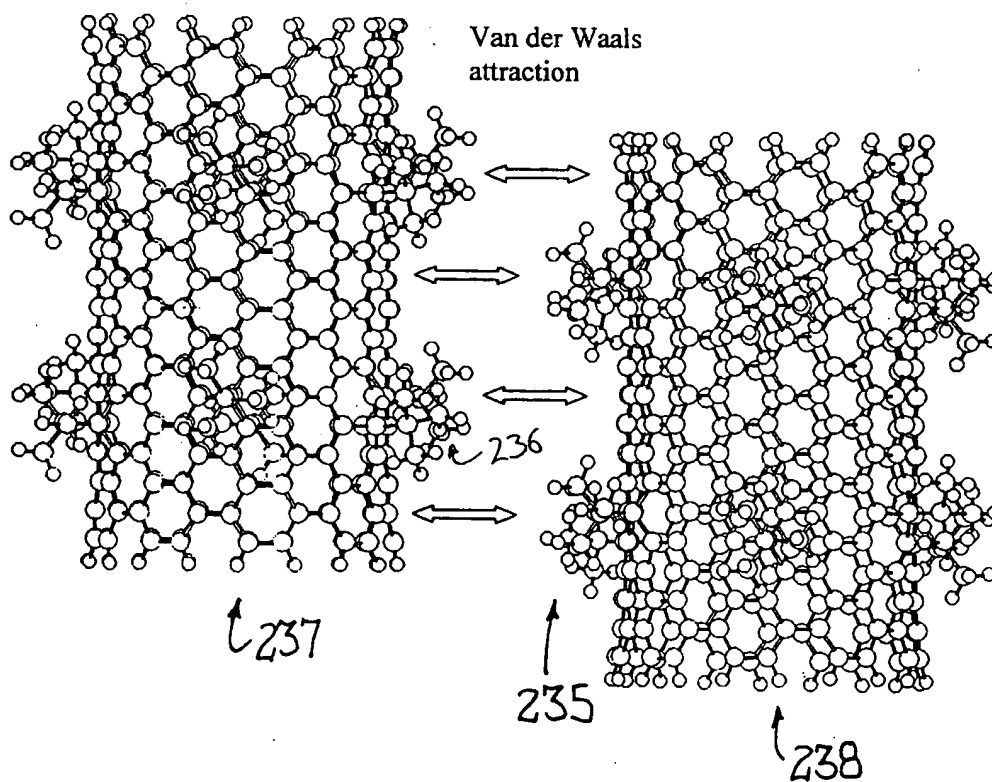


FIG. 36



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/00204

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C01B 31/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC: C01B 31/02; H01L; C30B 29/		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT: (NANOWIR: OR NANOTUB: OR BUCKYTUB: OR NANOSELECT: OR NANOTECHNOL: OR SWNT: OR NANOFABRICAT:) CHEM ABS: (NANOWIRES OR FABRICATION OR CONSTRUCTED OR JOINING OR UNITS)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95/00440 A (WILLIAM MARSH RICE UNIVERSITY) 5 January 1995	
A	US 5223479 A (McCAULEY, Jr et al) 29 June 1993	
A	Derwent Abstract Accession No: 95-272688/36, Class E36, L02, JP 07172807 A (NEC CORP) 11 July 1995	
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 11 May 1999		Date of mailing of the international search report 25 MAY 1999
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer J DEUIS Telephone No.: (02) 6283 2146

INTERNATIONAL SEARCH REPORT

In national application No.
PCT/AU 99/00204

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See attached sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/00204

Box II (continued)

The International application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. In coming to this conclusion the International Searching Authority has found that there are eleven inventions:

- 1 Claims 1, 10, 27 are directed to a structure and method of making that structure wherein the method comprises the steps of:
 - (a) bringing a series of intermediate parts together in a collation of intermediate parts;
 - (b) agitating said collation to an average energy exceeding said intermediate binding energy;
 - (c) slowly lowering said average energy to a level substantially at said first intermediate binding potential energy;
 - (d) introducing a catalytic element to said collation to cause said parts to bind at substantially said second lower potential energy so as to form said structure. It is considered that the above integers comprise a first "special technical feature".
- 2 Claim 11 is directed to a nanotube structure comprising a matrix of interconnected tetrahedral or cubic nanotube junctions. It is considered that the above integers comprise a second "special technical feature".
- 3 Claim 13 is directed to a nanotube structure comprising a series of nanotube interconnected with fullerene interconnection components. It is considered that the above integers comprise a third "special technical feature".
- 4 Claim 14 is directed to a method of constructing nanotube components interconnected to a buckyball or other hub component. It is considered that the above integers comprise a fourth "special technical feature".
- 5 Claim 15 is directed to a method of constructing a hub component for interconnecting multiple nanotube components. It is considered that the above integers comprise a fifth "special technical feature".
- 6 Claim 16 is directed to a method of constructing a low-density nanotube crystal. It is considered that the above integers comprise a sixth "special technical feature".
- 7 Claims 17, 18, 19, 20, 22 are directed to electrical devices comprising nanotubes of a zigzag-type interconnected with armchair-type nanotube(s). It is considered that the above integers comprise a seventh "special technical feature".
- 8 Claim 23 is directed to an electrical device comprising a series of armchair-type nanotubes interconnected to a common junction. It is considered that the above integers comprise an eighth "special technical feature".

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International Application No.
PCT/ AU 99/00204

Supplemental Box

(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

- 9 Claim 24 is directed to an electrical device comprising the interconnection of a labyrinth of nanotube devices via common junctions, said devices including a series of diode elements formed from the interconnection of nanotubes of different dimensions. It is considered that the above integers comprise a ninth "special technical feature".
- 10 Claim 25 is directed to an electrical device comprising a quantum well structure including the junction of a series of metallic-type nanotube structures attached to a semiconductive nanotube so that electrons are substantially captured in said junction. It is considered that the above integers comprise a tenth "special technical feature".
- 11 Claim 26 is directed to an electric device comprising a ballistic electron nanotube device including a nanotube junction with at least one quantum well structure adjacent the junction. It is considered that the above integers comprise an eleventh "special technical feature".

Since the above mentioned groups of claims do not share either technical features identified, a "technical relationship" between the inventions, as defined in PCT rule 13.2 does not exist. Accordingly, the International application does not relate to one invention as a single inventive concept.

Information on patent family members

PCT/AU 99/00204

particulars which are merely given for the purpose of information.

END OF ANNEX